

**LUBRICATING COMPOSITION INCLUDING ESTERIFIED
COPOLYMER AND LOW DISPERSANT LEVELS SUITABLE
FOR DRIVELINE APPLICATIONS**

FIELD OF INVENTION

[0001] The present embodiment relates to a lubricating composition comprising an esterified copolymer formed from a vinyl aliphatic monomer and an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof. The lubricating composition may further include an oil of lubricating viscosity. The copolymer serves as a dispersant in the lubricating composition for dispersing oxidation products generated during operation of the mechanical device, obviating the need for any other dispersants of the type conventionally used in driveline applications. The lubricating composition finds application in vehicle driveline systems, such as for an automotive gear oil. The invention further provides a method and use of the lubricating composition by supplying it to a driveline component of a vehicle, such as a gear box.

BACKGROUND

[0002] Lubricants for driveline power transmitting devices (such as gears or transmissions), especially automatic transmission fluids (ATFs), and manual transmission fluids (MTFs), and axle fluids, present challenges in satisfying lubricating requirements, whilst providing durability and cleanliness.

[0003] Lubricants have conventionally been prepared with polyalphaolefins, or bright stock (lubricating oils of high viscosity, obtained from the residues of petroleum distillation). To impart the desired viscometric properties in lubricants, viscosity index improvers, sometimes referred to as viscosity modifiers, have been added to lubricating oil compositions to change the viscosity index. Typical viscosity index improvers for gear oils include oil soluble polyisobutylenes, low molecular weight polymers of methacrylates and acrylates, olefin copolymers, and polyalphaolefins, such as PAO 100. When subject to high shear and high temperature, such lubricating oils can undergo oxidation. The byproducts of the oxidation can be harmful to driveline components, particularly since the lubricating oils are seldom, if ever replaced. Thus, a dispersant is commonly added to the lubricant. Dispersants attach themselves to contaminant particles

and hold them in suspension, thereby reducing deposition of the oxidation products. Conventional dispersants include ashless-type dispersants such as N-substituted long chain alkenyl succinimides, polyisobutylene succinimide complexed with zinc, Mannich bases, and post-treated dispersants formed by borating these compounds.

[0004] International Application WO2007/133999 discloses a polymer with pendent groups which may be a copolymer of an α -olefin and an unsaturated diacid or an anhydride thereof. The polymers may incorporate ester functionality in pendent groups. The ester functional groups may be derived from linear or branched alkyl alcohols. The polymers of WO 2007/133999 are said to be useful in a lubricant to provide at least one of acceptable dispersancy properties, acceptable shear stability, acceptable viscosity index control, and acceptable low temperature viscosity.

[0005] Examples of other polymers are disclosed in U.S. Patent Nos. 5,435,928; 6,174,843; 6,419,714; 6,544,935; and 7,254,249; and in International Application No. WO 2010/014655.

[0006] U.S. Patent No. 5,188,745 discloses a lubricating oil composition which includes an additive composition comprising a graft and derivatized copolymer prepared by reacting ethylene and at least one C₃-C₁₀ alpha-monoolefin and, optionally, a polyene selected from non-conjugated dienes and trienes, which has been reacted with at least one olefinic carboxylic acid acylating agent to form one or more acylating reaction intermediates having a carboxylic acid acylating function within their structure and by reacting the reaction intermediate with a N-(2-aminoalkyl)imidizolidone to form the graft derivatized copolymer.

[0007] The exemplary embodiment provides a lubricating composition with oxidative stability and improved cleanliness which can be achieved with only low amounts of a dispersant or without the use of a dispersant, other than an esterified copolymer as disclosed herein.

BRIEF DESCRIPTION

[0008] In accordance with one aspect of the exemplary embodiment, a lubricating composition includes an esterified copolymer including a backbone comprising units derived from a vinyl aliphatic monomer and units derived from a carboxylic acid monomer, the carboxylic acid monomer comprising an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof. The lubricating composition also includes an oil of lubricating viscosity. The lubricating composition comprises no more than 2.5 wt. % of dispersant for dispersing oxidation products, other than the esterified copolymer.

[0009] In another aspect, a process for preparing a lubricating composition includes forming an esterified copolymer, including (1) reacting (i) a vinyl aliphatic monomer and (ii) a carboxylic acid monomer comprising an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof, to form a copolymer, wherein the carboxylic acid monomer optionally has ester groups, (2) optionally, esterifying the copolymer of step (1) to form an esterified copolymer, and (3) optionally, reacting the copolymer of step (1) or (2) with a nitrogen-containing compound in an amount to provide an esterified copolymer with at least 0.01 wt. % nitrogen; and whereby the resulting copolymer is esterified in at least one of (1), (2), and (3) and mixing the esterified copolymer thus formed with at least one of an oil of lubricating viscosity and a performance additive other than the esterified copolymer, to provide a lubricating composition comprising no more than 2.5 wt. % of dispersant, other than the esterified copolymer, for dispersing oxidation products.

DETAILED DESCRIPTION

[0010] The present embodiment relates to a lubricating composition comprising an esterified copolymer as disclosed herein ("copolymer") which includes units derived from a polymerizable vinyl aliphatic monomer and units derived from an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof (referred to herein collectively as a carboxylic acid monomer). In one embodiment, the exemplary copolymer is capable of reducing the effects of oxidation of the lubricating composition, when used in a mechanical device. In

one embodiment, the copolymer is useful as a base oil replacement in the lubricating composition. Other aspects relate to a method for lubricating a mechanical device with the lubricating composition. The exemplary mechanical device is a vehicle driveline device including a gear or transmission system.

[0011] The lubricating composition is substantially free of dispersants. By “substantially free” it is meant that the lubricating composition, as formulated for use in a driveline system, includes no more than a total of 2.5 wt. % of all dispersants, other than the exemplary esterified copolymer, which provide for dispersion of oxidation products generated during use of the lubricating composition in a mechanical device. For example, the lubricating composition may include from 0-2.5 wt. % of such dispersant(s), other than the exemplary copolymer, or no more than 2 wt. %, or no more than 1.75 wt. %, or no more than 1.5 wt. %, or no more than 1 wt. %, or no more than 0.5 wt. %, or no more than 0.25 wt. %, or no more than 0.2 wt. %, or no more than 0.1 wt. %, or no more than 0.01 wt. % of such dispersant(s). The amount of dispersant excludes any oil or other diluent with which it may be mixed prior to incorporation of the dispersant into the composition. In one embodiment, the lubricating composition is dispersant free, by which it is meant that the lubrication composition contains no added dispersant, although a dispersant may be present in trace amounts of up to 0.001 wt.% or up to 0.0001 wt.% of the lubricating composition.

[0012] By “dispersant,” it is meant any of the performance additives commonly added to lubricating oils for their dispersancy characteristics, in particular, for dispersing oxidation products generated in the lubricating composition during operation of a mechanical device, such as a gear or transmission system. Such dispersants include ashless-type dispersants such as N-substituted long chain alkenyl succinimides, polyisobutylene succinimide complexed with zinc, Mannich bases, acylated polyalkylene polyamines, and post-treated dispersants formed by borating these compounds. By “long chain” it is meant a chain of at least 6, or at least 12, or 24, or 30 carbon atoms. Examples of such dispersants are given below, with the understanding that the total of all such dispersants is limited to the

amounts provided herein, and in one embodiment, that they are entirely absent from the exemplary lubricating composition (other than as trace amounts).

[0013] The term "copolymer," as used herein, generally refers to a polymer derived from two or more different monomers. The exemplary copolymer has a backbone which is derived from two (or more) different monomers.

[0014] The exemplary esterified copolymer disclosed herein includes a polymeric backbone which includes units derived from the vinyl aliphatic monomer and units derived from the carboxylic acid monomer. The backbone can be a chain comprising units derived from the selected monomers that are linked together such that the backbone comprises a chain of at least 10 such units, or at least 20 or at least 50 such monomer units. In one embodiment, the backbone chain of monomer units derived from the selected monomers is of no more than 1000 such monomer units, or no more than 500 such monomer units, or no more than 200 such monomer units. In the exemplary copolymer, a majority of the backbone, (such as at least 60%, or at least 70%, or at least 80%, or at least 90%, or at least 95%, such as 70%-95%, and up to 100% of the units in the backbone), is derived from the vinyl aliphatic monomer and the carboxylic acid monomer. Pendent groups may be grafted to the backbone, such as by esterification and/or amidization/imidization of the units of the backbone that are derived from the carboxylic acid monomer.

[0015] The polymeric backbone of the copolymer may be a generally alternating structure whereby each carboxylic acid unit (or at least a majority thereof) is spaced from the next carboxylic acid unit by at least one vinyl aliphatic monomer unit, each carboxylic acid unit being derived from a carboxylic acid monomer which can be the same or different, and wherein each vinyl aliphatic monomer unit can be derived from the same or a different vinyl aliphatic monomer. A molar ratio of the vinyl aliphatic monomer units to carboxylic acid monomer units in the copolymer can be for example, from 1:3 to 3:1 or from 0.6:1 to 1.2:1. In one embodiment, the molar ratio is about 0.7:1 to 1:1.1 in the copolymer. It is to be appreciated, however, that the molar ratios used in the preparation of the copolymer may differ from those in the copolymer.

Additionally, when units of a third monomer are present in the copolymer, the ratio of the vinyl aliphatic monomer units to carboxylic acid monomer units may be modified slightly to accommodate these units.

[0016] In one embodiment, the backbone chain comprising units derived from the selected monomers may further comprise units derived from a vinyl aromatic monomer, such that, for example, no more than 25%, or no more than 15%, or no more than 10% or no more than 5% of the monomer units of the backbone chain are derived from the vinyl aromatic monomer.

[0017] The exemplary copolymer further includes an ester group formed, for example, by esterification of at least some of the carboxylic acid units of the copolymer with a primary alcohol, such as one or more of a linear alcohol and a branched alcohol.

[0018] The exemplary esterified copolymer further includes a nitrogen containing group (such as amino-, amido- and/or imido- group) formed, for example, from a nitrogen containing compound capable of being incorporated during copolymerization. In one embodiment, the nitrogen containing group forms a salt of the carboxylic acid unit, for example, by reaction of the carboxylic acid unit with an amine without driving off water.

[0019] A process for forming the exemplary lubricating composition can comprise the steps of: (A) forming an esterified copolymer with nitrogen-containing groups and (B), mixing the esterified copolymer formed in (A) with at least one of (i) an oil of lubricating viscosity and (ii) a performance additive, other than the exemplary copolymer. Step (A) may include:

- (1) reacting (i) a vinyl aliphatic monomer, such as an α -olefin (and optionally, a vinyl aromatic monomer, such as styrene), and (ii) a carboxylic acid monomer, such as maleic acid or a derivative thereof, such as maleic anhydride, to form a copolymer; wherein the carboxylic acid monomer optionally has ester groups, e.g., derived from a primary alcohol;
- (2) optionally, esterifying the copolymer of step (1), e.g., with a primary alcohol, to form an esterified copolymer; and

- (3) optionally, reacting the copolymer of step (2) with a nitrogen-containing compound, such as amine, in an amount to provide the esterified copolymer with, for example, 0.01 wt. % to 1.5 wt. % (or 0.05 wt. % to 0.75 wt. %, or 0.075 wt. % to 0.25 wt. %) nitrogen; and
- wherein the copolymer is esterified, e.g., in one or more of steps (1), (2), and (3).

[0020] In one embodiment, each of steps (1), (2), and (3) is performed. In this embodiment, the carboxylic acid monomer used in step (1) need not have ester groups.

[0021] In another embodiment, the carboxylic acid monomer may be esterified, e.g., with a primary alcohol prior to step (1), and step (2) may be omitted.

[0022] In another embodiment, steps (1) and (3) are performed and the nitrogen-containing compound provides the ester groups, in which case, step (2) may be omitted.

[0023] In another embodiment, the esterified copolymer is substantially free of a nitrogen-containing group, i.e., contains no more than 0.01 wt. % nitrogen.

[0024] By way of example, the exemplary copolymer can include a polymeric backbone of poly(alpha-olefin maleic anhydride), derived from 1-dodecene, as the vinyl aliphatic monomer, and maleic anhydride, as the carboxylic acid monomer, which is esterified with one or more primary alcohols by which pendent groups are grafted to the backbone to provide an esterified copolymer (poly(alpha-olefin maleic anhydride diester)) and which has been reacted with a nitrogen-containing compound (such as 4-(3-aminopropyl)morpholine or 1-(2-aminoethyl)imidazolidinone) to provide the esterified copolymer with from 0.01-1.5 wt. %, such as 0.05-0.2 wt. % nitrogen.

[0025] A lubricating composition ("oil") can be formed by admixing the exemplary copolymer with (i) an oil of lubricating viscosity (which may be referred to herein as a base oil), and optionally (ii) one or more other

performance additives (other than dispersants at more than the amounts specified herein).

[0026] A lubricating composition can also be formed by admixing the exemplary copolymer with one or more other performance additives (other than dispersants at more than the amounts specified herein), in the absence of an oil of lubricating viscosity.

[0027] The lubricating composition can include 5-75 wt. % of the exemplary copolymer, or 10-60 wt. %, or 30-60 wt. %, or 40-50 wt. %. Example lubricating compositions include 5-30 wt. %, or 5-20 wt. %, or 5-15 wt. %, or 5-10 wt. %, or 20-40 wt. % of the exemplary copolymer.

[0028] Weight average molecular weight (M_w) as used herein, is measured by gel permeation chromatography (GPC), also known as size-exclusion chromatography, employing a polystyrene standard. Typically the weight average molecular weight is measured on the final esterified copolymer, optionally reacted with a nitrogen-containing compound. The M_w of the exemplary polymer, before esterification, can range from 3000 to 50,000, and in one embodiment, may be 3000 to 20,000, such as at least 10,000.

[0029] The M_w of the exemplary polymer, after esterification and optional reaction with the nitrogen-containing compound, can range from 5000 to 50,000, and in one embodiment, may be 5000 to 25,000, or 10,000 to 17,000, or 5000 to 10,000, or 12,000 to 18,000, or 9,000 to 15,000, or 15,000 to 20,000.

[0030] The viscosity of the copolymer (e.g., in a lubricating composition) can be determined under ambient conditions, at low temperature (Brookfield viscosity), or under shear conditions. The viscosity shear stability index (SSI) of transmission lubricants, which measures the stability of the copolymer in a lubricating composition under shear conditions, can be measured by a 20 hour KRL test (Volkswagen Tapered Bearing Roller Test), as set out in standard CEC L-45-99 and DIN 51350-6-KRL/C. The 20hr KRL SSI of the exemplary lubricating composition may be from 0-30 SSI, or 0-10 SSI, or 10-30 SSI (i.e., low permanent shear loss) under the CEC L-45-99 method, when subjected to tapered roller bearing shear (5000N, 1475 RPM, 60°C).

[0031] One method for assessing the ability of the exemplary copolymer to improve the dispersing of oxidized material is to evaluate the lubricating composition for oxidative stability. This may be performed by DKA oxidation testing using the method described in CEC L-48-00, Oxidation Stability of Lubricating Oils used in Automotive Transmissions by Artificial Ageing (Laboratory Test) available from the Coordinating European Council for the development of performance tests for fuels, lubricants, and other fluids (CEC). In the exemplary method, the tests are run using the oxidation procedure as described in CEC L-48-00 procedure B whereby air is passed through 100ml of oil at a rate of 5 liters/hour for 192 hours at 160°C. The results are expressed as the percentage increase in kinematic viscosity at 40°C (%KV40) and at 100°C (%KV100). Typically, lower values recorded for the % increase in KV100 indicate improved performance.

[0032] Additionally, a test which has been used to determine the dispersive condition of a lubricating composition, either a test oil which has been subjected to oxidation testing or one which has been used in field service, is to assess the relative undispersed sludge spot size of the oil which has been placed on an absorbent material. This method involves placing a measured drop of the oxidized oil (at room temperature), onto the center of a filter paper using a disposable pipette and allowing the spot to develop. The filter paper is placed in a drying oven at 80°C (± 10°C) for one hour (± 15 minutes). The dispersed oil sample appears as a circular spot on the absorbent material whilst any undispersed sludge may appear as a darker inner circular spot. The dispersancy rating is calculated as:

$$\text{Dispersancy rating} = \frac{\text{diameter of the inner (non - dispersing sludge) spot}}{\text{Diameter of the outer dispersed spot}}$$

The Copolymer

A. The Vinyl Aliphatic Monomer Units

[0033] The copolymer includes vinyl aliphatic monomer units derived from a vinyl aliphatic monomer. An exemplary vinyl aliphatic monomer is a polymerizable aliphatic monomer, specifically, an aliphatic compound substituted with a vinyl group ($-\text{CH}=\text{CH}_2$). Examples of vinyl aliphatic monomers include

alpha-olefins selected from C₆-C₃₀ alpha-olefins such C₈-C₂₀ alpha-olefins, or C₁₀-C₁₈ alpha-olefins, or C₁₀-C₁₄ alpha-olefins. The alpha-olefin can be linear or branched. Examples of suitable linear alpha-olefins include 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene 1-octadecene, and mixtures thereof. An example of a useful vinyl aliphatic monomer is 1-dodecene.

B. The Carboxylic Acid Monomer Units

[0034] The α,β -ethylenically unsaturated carboxylic acid or derivative thereof used in forming the carboxylic acid units of the copolymer may be a dicarboxylic acid or an anhydride or other derivative thereof that may be wholly esterified, partially esterified, or a mixture thereof. When partially esterified, other functional groups may include acids, salts or mixtures thereof. Suitable salts include alkali metals, alkaline earth metals, and mixtures thereof. The salts may include lithium, sodium, potassium, magnesium, calcium or mixtures thereof.

[0035] Exemplary unsaturated carboxylic acids or derivatives thereof which may be used in forming the carboxylic acid units of the copolymer include acrylic acid, methyl acrylate, methacrylic acid, maleic acid, fumaric acid, itaconic acid, alpha-methylene glutaric acid, and anhydrides and mixtures thereof, and substituted equivalents thereof. Suitable examples of monomers for forming the carboxylic acid unit include itaconic anhydride, maleic anhydride, methyl maleic anhydride, ethyl maleic anhydride, dimethyl maleic anhydride, and mixtures thereof. In one embodiment, the carboxylic acid unit includes units derived from maleic anhydride or derivatives thereof.

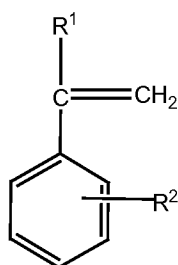
[0036] In the exemplary unsaturated carboxylic acids or derivatives thereof, a carbon-to-carbon double bond is typically in an alpha, beta-position relative to at least one of the carboxy functions (e.g., in the case of itaconic acid, anhydride or esters thereof) and may be in an alpha, beta-position to both of the carboxy functions of an alpha, beta-dicarboxylic acid, anhydride or the ester thereof (e.g., in the case of maleic acid or anhydride, fumaric acid, or ester thereof). In one embodiment, the carboxy functions of these compounds will be separated by up to 4 carbon atoms, such as 2 carbon atoms.

[0037] Other suitable monomers for forming the carboxylic acid monomer unit of the exemplary copolymer are described in U.S. Pub. No. 20090305923.

C. Optional Units

[0038] In one embodiment, the backbone chain, in addition to the vinyl aliphatic monomer units and carboxylic monomer units, may further include other monomer-derived units capable of polymerizing with one or both of the vinyl aliphatic monomer units and carboxylic monomer units. These additional units may be randomly incorporated throughout the copolymer backbone or may be in the form of a block or blocks. The copolymer may comprise in total, up to 30 mole %, or up to 20 mole %, or up to 10 mole % of such optional units. As an example of such optional units are derived from a vinyl aromatic monomer or (meth)acrylate. An exemplary vinyl aromatic monomer, where present, is a polymerizable aromatic monomer, specifically, an aromatic compound substituted with a vinyl group ($-\text{CH}=\text{CH}_2$).

[0039] Suitable vinyl aromatic monomers are those corresponding to Formula I:



Formula I:

wherein R^1 and R^2 independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or a halogen containing group. The vinyl aromatic monomer may be selected from styrene, alpha-alkylstyrenes, nuclear alkylstyrenes, chlorostyrenes, dichlorostyrenes, vinyl naphthalene, and mixtures of these. Specific examples include styrene, alpha-methylstyrene, alpha-ethylstyrene, alpha-isopropylstyrene, alpha-tert-butylstyrene, nuclear alkylstyrenes such as *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, *o*-methyl-alpha-methylstyrene, *m*-methyl-alpha-methylstyrene, *p*-methyl-alpha-

methylstyrene, *m*-isopropyl- α -methylstyrene, *p*-isopropyl- α -methylstyrene, *m*-isopropylstyrene, *p*-isopropylstyrene, vinylnaphthalene, and mixtures thereof.

D. Alcohols for Esterification of the Carboxylic Acid Unit

[0040] The carboxylic acid unit of the copolymer may be wholly or partially esterified with a primary alcohol. The ester groups are usually formed by reacting the carboxy-containing copolymer with alcohols, although in some embodiments, especially for lower alkyl esters, the ester group may be incorporated from one of the monomers used to prepare the copolymer.

[0041] Suitable primary alcohols for use herein may contain 8 to 60, or 8 to 40, or 8 to 24, or 8-16 carbon atoms, such as 8-10 carbon atoms. The primary alcohol may be linear or may be branched at the α - or β - or higher position. In one embodiment, a mixture of linear and branched alcohols is employed in forming the esterified copolymer described herein. In one exemplary embodiment, at least 0.1 % of the carboxylic acid units in the copolymer are esterified with an alcohol branched at β - or higher position.

[0042] In one embodiment, 20 to 100 mole %, or 30 to 100 mole %, or 30 to 70 mole %, based on the total number of moles of carboxyl groups in the copolymer contain ester groups having 12 to 19 carbon atoms in the alcohol group (that is, in the alcohol-derived or alkoxy portion of the ester) and 70 or 80 to 100 mole %, alternatively 80 to 30 mole %, based on the total number of moles of carboxyl groups in the copolymer, contain ester groups having 8 to 10 carbon atoms in the alcohol portion. In one embodiment, the esterified copolymer contains at least 45 mole %, based on moles of carboxyl groups in the esterified copolymer, of ester groups containing from 12 to 18 carbon atoms in the alcohol portion. In an optional embodiment, the esterified copolymer has up to 20 mole % or 0 to 5% or 1 to 2%, based on the total number of moles of carboxyl groups in the copolymer, of ester groups having from 1 to 6 carbon atoms in the alcohol portion. In one embodiment, the compositions are substantially free of ester groups containing from 3 to 7 carbon atoms.

[0043] In one embodiment, 0.1 to 99.99 (or 1 to 50, or 2.5 to 20, or 5 to 15) percent of the carboxylic acid units esterified are esterified with a primary alcohol

branched at the β - or higher position, 0.1 to 99.89 (or 1 to 50, or 2.5 to 20, or 5 to 15) percent of the carboxylic acid units esterified are esterified with a linear alcohol or an alpha-branched alcohol, and 0.01 to 10 % (or 0.1 % to 20 %, or 0.02 % to 7.5 %, or 0.1 to 5 %, or 0.1 to less than 2 %) of the carboxylic acid units has at least one nitrogen-containing group, such as an amino-, amido- and/or imido-group, and/or a salt formed between the amine and the carboxylic acid, as described below. As an example, 5 to 15 percent of the carboxylic acid units of the copolymer are esterified with a primary alcohol branched at the β - or higher position, 0.1 to 95 percent of the carboxylic acid units are esterified with a linear alcohol or an alpha-branched alcohol, and 0.1 to less than 2% of the carboxylic acid units has at least one nitrogen-containing group.

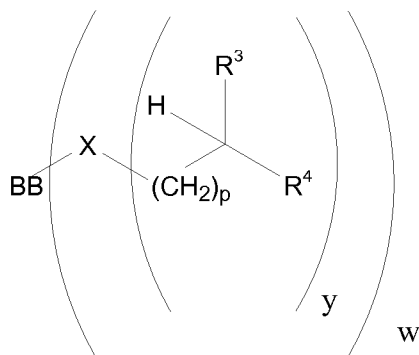
[0044] Examples of useful primary alcohols include butanol, heptanol, octanol, 2-ethylhexanol, decanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, and combinations thereof.

[0045] Other exemplary primary alcohols include commercially available mixtures of alcohols. These include oxoalcohols which may comprise, for example, various mixtures of alcohols having from 8-24 carbon atoms. Of the various commercial alcohols useful herein, one contains 8 to 10 carbon atoms, and another 12 to 18 aliphatic carbon atoms. The alcohols in the mixture may include one or more of, for example, octyl alcohol, decyl alcohol, dodecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, and octadecyl alcohol. Several suitable sources of these alcohol mixtures are the technical grade alcohols sold under the name NEODOL® alcohols (Shell Oil Company, Houston, Tex.) and under the name ALFOL® alcohols (Sasol, Westlake, La.), and fatty alcohols derived from animal and vegetable fats and sold commercially by, for example, Henkel, Sasol, and Emery.

[0046] Tertiary alkanolamines, i.e., N,N-di-(lower alkyl)amino alkanolamines, are other alcohols that may be used to prepare the esterified copolymers. Examples include N,N-dimethylethanolamine, N,N-diethylethanolamine, 5-diethylamino-2-pentanol, and combinations thereof.

[0047] Exemplary primary alcohols branched at the β - or higher position may include Guerbet alcohols. Methods to prepare Guerbet alcohols are disclosed in U.S. Patent No. 4,767,815 (see column 5, line 39 to column 6, line 32).

[0048] The primary alcohol branched at the β - or higher position may be used to provide pendent groups as represented within ()_w of the Formula II:



Formula II

wherein

(BB) is a copolymer backbone comprising the carboxylic acid monomer units and vinyl aliphatic monomer units.

X is a functional group which either (i) contains a carbon and at least one oxygen or nitrogen atom or (ii) is an alkylene group with 1 to 5 carbon atoms (typically $-CH_2-$), connecting the copolymer backbone and a branched hydrocarbyl group contained within ()_y;

w is the number of pendent groups attached to the copolymer backbone, which may be in the range of 2 to 2000, or 2 to 500, or 5 to 250;

y is 0, 1, 2 or 3, provided that in at least 1 mol. % of the pendent groups, y is not zero; and with the proviso that when y is 0, X is bonded to a terminal group in a manner sufficient to satisfy the valence of X, wherein the terminal group is selected from hydrogen, alkyl, aryl, a metal (typically introduced during neutralization of ester reactions. Suitable metals include calcium, magnesium, barium, zinc, sodium, potassium or lithium) or ammonium cation, and mixtures thereof;

p is an integer in the range of 1 to 15 (or 1 to 8, or 1 to 4);

R^3 and R^4 are independently linear or branched hydrocarbyl

groups, and the combined total number of carbon atoms present in R^3 and R^4 is at least 12 (or at least 16, or at least 18 or at least 20).

[0049] In different embodiments, the copolymer with pendent groups may contain 0.10% to 100%, or 2% to 20%, such as 5% to 20%, or 10% to 18%, branched hydrocarbyl groups represented by a group within ()_y of the Formula II, expressed as a percentage of the total number of pendent groups. The pendent groups of Formula II may also be used to define the ester groups as defined above by the phrase “a primary alcohol branched at the β - or higher position”.

[0050] In different embodiments the functional groups defined by X in Formula II above, may comprise at least one of $-\text{CO}_2^-$, $-\text{C}(\text{O})\text{N}=\text{}$ or $-(\text{CH}_2)_v-$, wherein v is an integer in the range of 1 to 20, or 1 to 10, or 1 to 2.

[0051] In one embodiment, X is derived from an α,β -ethylenically unsaturated dicarboxylic acid or derivatives thereof. Examples of a suitable carboxylic acid or derivatives thereof typically include maleic anhydride, maleic acid, (meth)acrylic acid, itaconic anhydride or itaconic acid. In one embodiment, the α,β -ethylenically unsaturated dicarboxylic acid or derivative(s) thereof may be at least one of maleic anhydride or maleic acid.

[0052] In one embodiment X is other than an alkylene group, connecting the copolymer backbone and the branched hydrocarbyl groups.

[0053] In different embodiments the pendent groups may be esterified, amidated or imidated functional groups.

[0054] Examples of suitable groups for R^3 and R^4 in Formula II include: alkyl groups containing C_{15-16} polymethylene groups, such as 2- C_{1-15} alkyl-hexadecyl groups (e.g., 2-octylhexadecyl) and 2-alkyl-octadecyl groups (e.g., 2-ethyloctadecyl, 2-tetradecyl-octadecyl and 2-hexadecyloctadecyl); alkyl groups containing C_{13-14} polymethylene groups, such as 1- C_{1-15} alkyl-tetradecyl groups (e.g., 2-hexyltetradecyl, 2-decyltetradecyl and 2-undecyltridecyl) and 2- C_{1-15} alkyl-hexadecyl groups (e.g., 2-ethyl-hexadecyl and 2-dodecylhexadecyl); alkyl groups containing C_{10-12} polymethylene groups, such as 2- C_{1-15} alkyl-dodecyl groups (e.g., 2-octyldodecyl) and 2- C_{1-15} alkyl-dodecyl groups (2-hexyldodecyl and 2-octyldodecyl), 2- C_{1-15} alkyl-tetradecyl groups (e.g., 2-hexyltetradecyl and 2-decyltetradecyl); alkyl groups containing C_{6-9} polymethylene groups, such as 2-

C₁₋₁₅ alkyl-decyl groups (e.g., 2-octyldecyl) and 2,4-di-C₁₋₁₅ alkyl-decyl groups (e.g., 2-ethyl-4-butyl-decyl); alkyl groups containing C₁₋₅ polymethylene groups, such as 2-(3-methylhexyl)-7-methyl-decyl and 2-(1,4,4-trimethylbutyl)-5,7,7-trimethyl-octyl groups; and mixtures of two or more branched alkyl groups, such as alkyl residues of oxoalcohols corresponding to propylene oligomers (from hexamer to undecamer), ethylene/propylene (molar ratio 16:1-1:11) oligomers, isobutene oligomers (from pentamer to octamer), and C₅₋₁₇ α -olefin oligomers (from dimer to hexamer).

[0055] The pendent groups may contain a total combined number of carbon atoms on R³ and R⁴ in the range of 12 to 60, or 14 to 50, or 16 to 40, or 18 to 40, or 20 to 36.

[0056] Each of R³ and R⁴ may individually contain 5 to 25, or 8 to 32, or 10 to 18 methylene carbon atoms. In one embodiment, the number of carbon atoms on each R³ and R⁴ group may be 10 to 24.

[0057] In different embodiments, the primary alcohol branched at the β - or higher position may have at least 12 (or at least 16, or at least 18 or at least 20) carbon atoms. The number of carbon atoms may range from at least 12 to 60, or at least 16 to 30.

[0058] Examples of suitable primary alcohols branched at the β - or higher position include 2-ethylhexanol, 2-butyloctanol, 2-hexyldecanol, 2-octyldodecanol, 2-decyltetradecanol, and mixtures thereof.

E. Nitrogen-Containing Group

[0059] The exemplary esterified copolymer includes a nitrogen containing group, such as an amino-, amido- and/or imido- group. The nitrogen containing group may be derived from a nitrogen-containing compound capable of being incorporated during copolymerization (or through reaction with the carboxylic acid units to form a salt), such as an amine, amide, imide, or mixture thereof, e.g., through being aminated (which as used herein includes forming salts of the carboxylic acid units), amidated, and/or imidated with a nitrogen-containing compound.

[0060] Examples of suitable nitrogen-containing compounds capable of being incorporated into the copolymer include N,N-dimethylacrylamide, N-vinyl

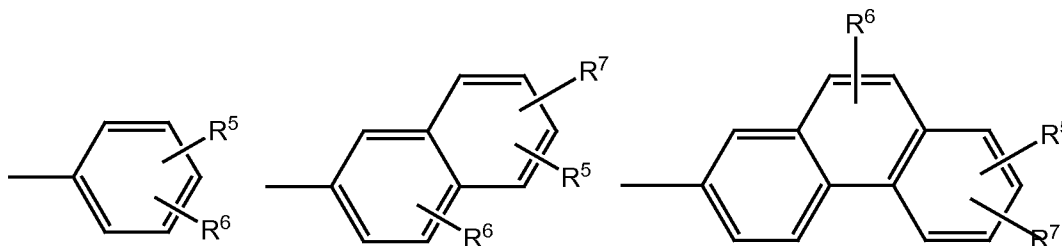
carbonamides, such as N-vinyl-formamide, N-vinylacetamide, N-vinyl propionamides, N-vinyl hydroxyacetamide, vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminobutyl acrylamide, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminoethyl acrylamide, and mixtures thereof.

[0061] The copolymer may include a nitrogen containing group that may be capable of reacting with the esterified copolymer backbone, typically for capping the copolymer backbone. The capping may result in the copolymer having ester, amide, imide and/or amine groups.

[0062] The nitrogen-containing group may be derived from a primary or secondary amine, such as an aliphatic amine, aromatic amine, aliphatic polyamine, aromatic polyamine, polyaromatic polyamine, or combination thereof.

[0063] In one embodiment, the nitrogen containing group may be derived from an aliphatic amine, such as a C₁-C₃₀ or C₁-C₂₄ aliphatic amine. Examples of suitable aliphatic amines include aliphatic monoamines and diamines, which may be linear or cyclic. Examples of suitable primary amines include methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, oleylamine, dimethylaminopropylamine, diethylaminopropylamine, dibutylaminopropylamine, dimethylaminoethylamine, diethylaminoethylamine, and dibutylaminoethylamine. Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine, diethylhexylamine, and ethylamylamine. The secondary amines may be cyclic amines such as aminoethylmorpholine, aminopropylmorpholine, 1-(2-aminoethyl)pyrrolidone, piperidine, 1-(2-aminoethyl)piperidine, piperazine and morpholine. Examples of suitable aliphatic polyamines include tetraethylene pentamine, pentaethylenhexamine, diethylenetriamine, triethylenetetramine, and polyethyleneimine.

[0064] In another embodiment, the nitrogen containing group may be derived from an aromatic amine. Aromatic amines include those which can be represented by the general structure $\text{NH}_2\text{-Ar}$ or T-NH-Ar , where T may be alkyl or aromatic, Ar is an aromatic group, including nitrogen-containing aromatic groups and Ar groups including any of the following structures:

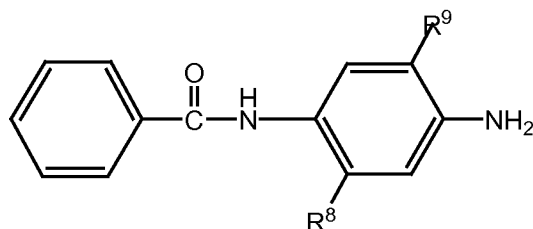


as well as multiple non-condensed or linked aromatic rings. In these and related structures, R^5 , R^6 , and R^7 can be independently selected from, among other groups disclosed herein, $-\text{H}$, $-\text{C}_{1-18}$ alkyl groups, nitro groups, $-\text{NH-Ar}$, $-\text{N=N-Ar}$, $-\text{NH-CO-Ar}$, $-\text{OOC-Ar}$, $-\text{OOC-C}_{1-18}$ alkyl, $-\text{COO-C}_{1-18}$ alkyl, $-\text{OH}$, $-\text{O}-(\text{CH}_2\text{CH}_2\text{-O})_n\text{C}_{1-18}$ alkyl groups, and $-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{Ar}$ (where n is 0 to 10).

[0065] Exemplary aromatic amines include those amines wherein a carbon atom of the aromatic ring structure is attached directly to the amino nitrogen. The aromatic amines may be monoamines or polyamines. The aromatic ring may be a mononuclear aromatic ring (i.e., one derived from benzene) but can include fused aromatic rings, especially those derived from naphthalene. Examples of aromatic amines include aniline, N-alkylanilines such as N-methylaniline and N-butylaniline, di-(para-methylphenyl)amine, 4-aminodiphenylamine, N,N-dimethylphenylenediamine, naphthylamine, 4-(4-nitrophenyl-azo)aniline (disperse orange 3), sulfamethazine, 4-phenoxyaniline, 3-nitroaniline, 4-aminoacetanilide (N-(4-aminophenyl)acetamide), 4-amino-2-hydroxy-benzoic acid phenyl ester (phenyl amino salicylate), N-(4-amino-phenyl)-benzamide, various benzylamines, such as 2,5-dimethoxybenzylamine, 4-phenylazoaniline, and combinations and substituted versions of these. Other examples include para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline. Examples of other suitable aromatic amines include amino-substituted aromatic compounds and amines in which the amine nitrogen is a part of an aromatic ring, such as 3-aminoquinoline, 5-

aminoquinoline, and 8-aminoquinoline. Also included are aromatic amines, such as 2-aminobenzimidazole, which contains one secondary amino group attached directly to the aromatic ring and a primary amino group attached to the imidazole ring. Other amines include N-(4-anilinophenyl)-3-aminobutanamide, and 3-amino propyl imidazole, and 2,5-dimethoxybenzylamine.

[0066] Additional aromatic amines and related compounds are disclosed in U.S. Patent Nos. 6,107,257 and 6,107,258. Examples of these include aminocarbazoles, benzoimidazoles, aminoindoles, aminopyrroles, amino-indazolinones, aminoperimidines, mercaptotriazoles, aminophenothiazines, aminopyridines, aminopyrazines, aminopyrimidines, pyridines, pyrazines, pyrimidines, aminothiadiazoles, aminothiothiadiazoles, and aminobenzotriazoles. Other suitable amines include 3-amino-N-(4-anilinophenyl)-N-isopropyl butanamide, and N-(4-anilinophenyl)-3-[(3-aminopropyl)-(cocoalkyl)amino] butanamide. Other aromatic amines which can be used include various aromatic amine dye intermediates containing multiple aromatic rings linked by, for example, amide structures. Examples include materials of the general structure:



and isomeric variations thereof, where R^8 and R^9 are independently alkyl or alkoxy groups such as methyl, methoxy, or ethoxy.

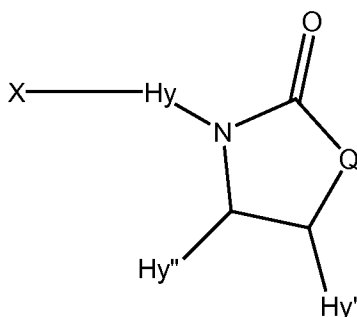
[0067] In one instance, R^8 and R^9 are both $-OCH_3$ and the material is known as Fast Blue RR [CAS# 6268-05-9]. In another instance, R^9 is $-OCH_3$ and R^8 is $-CH_3$, and the material is known as Fast Violet B [99-21-8]. When both R^8 and R^9 are ethoxy, the material is known as Fast Blue BB [120-00-3]. U.S. Patent No. 5,744,429 discloses other aromatic amine compounds useful herein, particularly aminoalkylphenothiazines. N-aromatic substituted acid amide compounds, such as those disclosed in U.S. Pub. No. 2003/0030033, may also be used herein. Suitable aromatic amines include those in which the amine nitrogen is a substituent on an aromatic carboxylic compound, that is, the nitrogen is not sp^2 hybridized within an aromatic ring.

[0068] The aromatic amine may have an N-H group capable of condensing with the pendent carbonyl-containing group. Certain aromatic amines are commonly used as antioxidants. Examples of these are alkylated diphenylamines, such as nonyldiphenylamine and dinonyldiphenylamine. To the extent that these materials will condense with the carboxylic functionality of the polymer chain, they are also suitable for use herein. However, it is believed that the two aromatic groups attached to the amine nitrogen reduce its reactivity. Thus, suitable amines include those having a primary nitrogen atom (-NH_2) or a secondary nitrogen atom in which one of the hydrocarbyl substituents is a relatively short chain alkyl group, e.g., methyl. Among such aromatic amines are 4-phenylazoaniline, 4-aminodiphenylamine, 2-aminobenzimidazole, and N,N-dimethylphenylenediamine. Some of these and other aromatic amines may also impart antioxidant performance to the copolymers, in addition to dispersancy and other properties.

[0069] In one embodiment, the amine component of the copolymer further includes an amine having at least two N-H groups capable of condensing with the carboxylic functionality of the copolymer. This material is referred to hereinafter as a "linking amine" as it can be employed to link together two of the copolymers containing the carboxylic acid functionality. It has been observed that higher molecular weight materials may provide improved performance, and this is one method to increase the material's molecular weight. The linking amine can be either an aliphatic amine or an aromatic amine; if it is an aromatic amine, it is considered to be in addition to and a distinct element from the aromatic amine described above, which typically will have only one condensable or reactive NH group, in order to avoid excessive crosslinking of the copolymer chains. Examples of such linking amines include ethylenediamine, phenylenediamine, and 2,4-diaminotoluene; others include propylenediamine, hexamethylenediamine, and other, ω -polymethylenediamines. The amount of reactive functionality on such a linking amine can be reduced, if desired, by reaction with less than a stoichiometric amount of a blocking material such as a hydrocarbyl-substituted succinic anhydride.

[0070] In one embodiment, the exemplary copolymer provides for oxidation control. Typically, the copolymer with oxidation control contains an incorporated residue of an amine-containing compound such as morpholines, pyrrolidinones, imidazolidinones, amino amides (such as acetamides), β -alanine alkyl esters, and mixtures thereof. Examples of suitable nitrogen-containing compounds include 3-morpholin-4-yl-propylamine, 3-morpholin-4-yl-ethylamine, β -alanine alkyl esters (typically alkyl esters have 1 to 30, or 6 to 20 carbon atoms), or mixtures thereof.

[0071] In one embodiment, the compounds based on imidazolidinones, cyclic carbamates or pyrrolidinones may be derived from a compound of general structure:



wherein

X = -OH or NH₂;

Hy'' is hydrogen, or a hydrocarbyl group (typically alkyl, or C₁₋₄-, or C₂-alkyl);

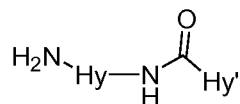
Hy is a hydrocarbylene group (typically alkylene, or C₁₋₄-, or C₂-alkylene);

Q = >NH, >NR, >CH₂, >CHR, >CR₂, or -O- (typically >NH, or >NR) and

R is C₁₋₄ alkyl.

[0072] In one embodiment, the imidazolidinone includes 1-(2-amino-ethyl)-imidazolidin-2-one (may also be called aminoethylethyleneurea), 1-(3-amino-propyl)-imidazolidin-2-one, 1-(2-hydroxy-ethyl)-imidazolidin-2-one, 1-(3-amino-propyl)-pyrrolidin-2-one, 1-(3-amino-ethyl)-pyrrolidin-2-one, or mixtures thereof.

[0073] In one embodiment, the amino amide includes an acetamide, which may be represented by the general structure:



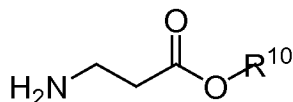
wherein:

Hy is a hydrocarbylene group (typically alkylene, or C₁₋₄-, or C₂- alkylene);
and

Hy' is a hydrocarbyl group (typically alkyl, or C₁₋₄-, or methyl).

[0074] Examples of a suitable acetamide include N-(2-amino-ethyl)-acetamide, or N-(2-amino-propyl)-acetamide.

[0075] In one embodiment, the β -alanine alkyl esters may be represented by the general structure:



wherein:

R¹⁰ is an alkyl group having 1 to 30, or 6 to 20 carbon atoms.

[0076] Examples of suitable β -alanine alkyl esters include β -alanine octyl ester, β -alanine decyl ester, β -alanine 2-ethylhexyl ester, β -alanine dodecyl ester, β -alanine tetradecyl ester, or β -alanine hexadecyl ester.

[0077] In one embodiment, the copolymer may be reacted with an amine selected from the group consisting of 1-(2-amino-ethyl)-imidazolidin-2-one, 4-(3-aminopropyl)morpholine, 3-(dimethylamino)-1-propylamine, N-phenyl-*p*-phenylenediamine, N-(3-aminopropyl)-2-pyrrolidinone, aminoethyl acetamide, β -alanine methyl ester, 1-(3-aminopropyl) imidazole, and mixtures thereof.

[0078] In one embodiment, the copolymer may be reacted with an amine-containing compound selected from morpholines, imidazolidinones, and mixtures thereof.

[0079] In one embodiment, the nitrogen-containing compound is selected from 1-(2-aminoethyl)imidazolidinone, 4-(3-aminopropyl)morpholine, 3-(dimethylamino)-1-propylamine, N-phenyl-*p*-phenylenediamine, N-(3-aminopropyl)-2-pyrrolidinone, aminoethyl acetamide, β -alanine methyl ester, 1-(3-aminopropyl) imidazole, and combinations thereof.

[0080] In one embodiment, the nitrogen-containing compound is a non-dispersing nitrogen compound having only a single reactive nitrogen group. Reactive nitrogen groups are primary or secondary nitrogen groups, i.e., nitrogen groups having at least one hydrogen atom on the nitrogen. For example, the nitrogen-containing compound is substantially free (i.e., no more than 2.5 mol %, or up to 0.1 mol%, or 0 mol %) of dispersing nitrogen-containing compounds, i.e., those having at least a second reactive nitrogen group, i.e., more reactive nitrogen group(s) than take part in the reaction with the esterified copolymer, which leaves reactive nitrogen groups on the resulting copolymer.

[0081] The ester group and/or nitrogen containing group may be sufficient to provide 0.01 wt. % to 1.5 wt. % (or 0.02 wt. % to 0.75 wt. %, or 0.04 wt. % to 0.25 wt. %, or 0.2 wt. % to 0.8 wt. %) nitrogen to the copolymer.

I. Preparation of the Copolymer

A. Formation of the Copolymer Backbone

[0082] The copolymer may optionally be prepared in the presence of a free radical initiator, solvent, or mixtures thereof. It will be appreciated that altering the amount of initiator can alter the number average molecular weight of the exemplary copolymer.

[0083] The copolymer backbone may be prepared by reacting the carboxylic acid monomer with the vinyl aliphatic monomer.

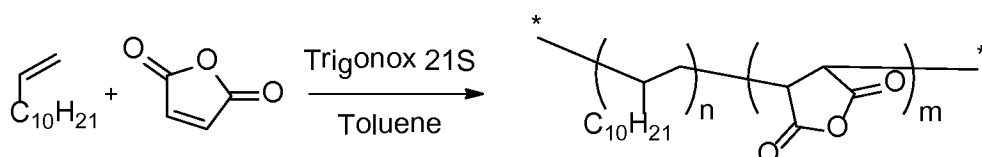
[0084] The solvent can be a liquid organic diluent. Generally, the solvent has a boiling point that is high enough to provide the required reaction temperature. Illustrative diluents include toluene, t-butyl benzene, benzene, xylene, chlorobenzene, various petroleum fractions boiling above 125°C, and mixtures thereof.

[0085] The free radical initiator can include one or more peroxy compounds, such as peroxides, hydroperoxides, and azo compounds which decompose thermally to provide free radicals. Other suitable examples are described in J. Brandrup and E. H. Immergut, Editor, "Polymer Handbook", 2nd edition, John Wiley and Sons, New York (1975), pages II-1 to II-40. Examples of a free radical initiator include those derived from a free radical-generating reagent, and examples include benzoyl peroxide, t-butyl perbenzoate, t-butyl

metachloroperbenzoate, t-butyl peroxide, sec-butylperoxydicarbonate, azobisisobutyronitrile, t-butyl peroxide, t-butyl hydroperoxide, t-amyl peroxide, cumyl peroxide, t-butyl peroctoate, t-butyl-m-chloroperbenzoate, azobisisovaleronitrile, and mixtures thereof. In one embodiment, the free radical generating reagent is t-butyl peroxide, t-butyl hydroperoxide, t-amyl peroxide, cumyl peroxide, t-butyl peroctoate, t-butyl-m-chloroperbenzoate, azobisisovaleronitrile, or mixtures thereof. Commercially available free radical initiators include classes of compound sold under the trademark Trigonox®-21 from Akzo Nobel.

[0086] An exemplary backbone polymer can be formed as follows: alpha-olefin is reacted with maleic anhydride in the presence of radical initiator and optionally in the presence of solvent. A solvent such as toluene can be used to lower backbone length by diluting the monomer concentration and through chain transfer to the benzylic protons. Scheme 1 shows an example where the alpha-olefin is 1-dodecene, the initiator is *tert*-butyl peroxy-2-ethylhexanoate (sold under the tradename Trigonox 21S by Akzo Nobel), and the solvent is toluene.

Scheme 1:



where n and m are independently at least 1, such as an integer from 1 to 10, or from 1 to 5, or from 1 to 3 in each segment of the copolymer (denoted by the two asterisks). As will be appreciated, the resulting backbone copolymer can have random variation of n and m .

B. Esterification

[0087] Esterification (or transesterification, when the copolymer already contains ester groups and those of a different type are desired) of the exemplary backbone copolymer can be accomplished by heating any of the copolymers described above and one or more desired alcohols and/or alkoxylates under conditions typical for effecting esterification. Such conditions include, for

example, a temperature of at least 80°C, such as up to 150°C or higher, provided that the temperature is maintained below the lowest decomposition temperature of any component of the reaction mixture or products thereof. Water or lower alcohol is normally removed as the esterification proceeds. These conditions may optionally include the use of a substantially inert, normally liquid, organic solvent or diluent such as mineral oil, toluene, benzene, xylene, or the like, and an esterification catalyst such as one or more of toluene sulfonic acid, sulfuric acid, aluminum chloride, boron trifluoride-triethylamine, methane sulfonic acid, trifluoro-methanesulfonic acid, hydrochloric acid, ammonium sulfate, and phosphoric acid. Further details of conducting the esterification can be found in U.S. Patent No. 6,544,935, at column 11.

[0088] In one embodiment, at least 75% of, or in certain embodiments at least 80%, or at least 90%, or 95% to 98% of the carboxy functions of the copolymer are esterified. Most or all of the remaining carboxy functions, which are unconverted to ester groups, will subsequently be converted to nitrogen-containing groups. An excess of alcohols and/or alkoxylates over the stoichiometric requirement for complete esterification of the carboxy functions may be used in the esterification process provided the ester content of the polymer remains in an appropriate range, e.g., within the 80 to 85% range. The excess of alcohols and alkoxylates or unreacted alcohols and alkoxylates need not be removed as such alcohols and alkoxylates can serve, for example, as diluent or solvent in the exemplary lubricating composition. Similarly, optional reaction media, e.g., toluene, need not be removed as they can similarly serve as diluent or solvent in the lubricating composition. In other embodiments, unreacted alcohols, alkoxylates and diluents are removed by well-known techniques, such as distillation.

[0089] Scheme 2 illustrates the case when the backbone copolymer of Scheme 1 is esterified. Esterification solubilizes the copolymer in oil and also improves the low temperature viscosity and improves the viscosity index of the lubricating composition including the esterified copolymer. The example shown uses a linear, primary C₈₋₁₀ alcohol mixture (available from Sasol under the trade name Alfol 810™) and 2-hexyl decan-1-ol (available

from Sasol under the trade name Isofol 16™), in methanesulfonic acid. R and R' are independently selected from linear C₈₋₁₀ alkyl and 2-hexyl decyl.

Scheme 2:



C. Formation of Nitrogen-containing Groups on the Copolymer Backbone

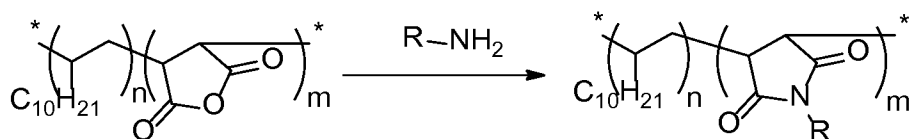
[0090] The nitrogen-containing compound may be directly reacted onto the copolymer backbone by grafting of the amine, or other nitrogen-containing functional group, onto the copolymer backbone either (i) in a solution using a solvent, or (ii) under reactive extrusion conditions in the presence or absence of solvent. The amine-functional monomer may be grafted onto the copolymer backbone in multiple ways. In one embodiment, the grafting takes place by a thermal process via an "ene" reaction. In one embodiment, the grafting takes place by a Friedel-Crafts acylating reaction. In another embodiment, the grafting is carried out in solution or solid form through a free radical initiator. Solution grafting is a well-known method for producing grafted copolymers. In such a process, reagents are introduced either neat or as solutions in appropriate solvents. The desired copolymer product may then be separated from the reaction solvents and/or impurities by appropriate purification steps.

[0091] In one embodiment, the nitrogen-containing compound may be directly reacted onto the copolymer backbone by free radical catalyzed grafting of the copolymer in a solvent, such as an organic solvent such as benzene, t-butyl benzene, toluene, xylene, hexane, or a combination thereof. The reaction may be carried out at an elevated temperature in the range of 100°C to 250°C or 120°C to 230°C, or 160°C to 200°C, e.g., above 160°C, in a solvent, such as a mineral lubricating oil solution containing, e.g., 1 to 50, or 5 to 40 wt. %, based

on the initial total oil solution of the copolymer and optionally under an inert environment.

[0092] By way of example, Scheme 3 exemplifies the consumption of residual anhydride groups in the backbone copolymer produced by Scheme 1, following the esterification in Scheme 2, using a primary amine(s). The functional group R in Scheme 3 can be selected to improve dispersancy.

Scheme 3:



[0093] In one embodiment, the amine can have more than one nitrogen and can be selected from aliphatic amines and aromatic amines such that the R group attached to the amine that reacts with the carboxylic acid monomer contains at least one nitrogen atom, optionally substituted with hydrocarbyl groups. The hydrocarbyl groups can be selected from aliphatic, aromatic, cyclic, and acyclic hydrocarbyl groups. As the amine, one or more of the following may be used: 1-(2-amino-ethyl)-imidazolidin-2-one, 4-(3-aminopropyl)morpholine, 3-(dimethylamino)-1-propylamine, N-phenyl-*p*-phenylenediamine, N-(3-aminopropyl)-2-pyrrolidinone, aminoethyl acetamide, β -alanine methyl ester, and 1-(3-aminopropyl) imidazole.

[0094] In another embodiment, the nitrogen-containing compound may be a monomer that can polymerize with both the vinyl aliphatic monomer and the carboxylic acid monomer such that the nitrogen-containing monomer is incorporated into the backbone. For example, a free radical catalyzed reaction is employed.

II. Lubricating Composition

[0095] In one embodiment, a lubricating composition includes an oil of lubricating viscosity and the exemplary copolymer comprising units derived from a vinyl aliphatic monomer and a carboxylic acid monomer as described above, which may have been esterified with a primary alcohol and may have been reacted with a nitrogen-containing compound, as described above. The

lubricating composition may include no more than 2.5 wt. % of dispersants, other than the exemplary copolymer, for dispersing oxidation products generated during use of the lubricating composition in a mechanical device.

[0096] The lubricating composition may include the oil of lubricating viscosity as a minor or major component thereof, such as at least 5 wt. %, or at least 20 wt. %, or at least 30 wt. %, or at least 40 wt. % of the lubricating composition. The lubricating composition suitable for use in a driveline system may include the oil of lubricating viscosity in an amount of at least 5 wt. % or at least 20 wt. % or at least 30 wt. % of the lubricating composition. In one embodiment, the oil of lubricating viscosity is no more than 60 wt. % of the lubricating composition.

[0097] In one embodiment, the esterified copolymer is 5-95 wt. %, or 10-60 wt. %, or 30-60 wt. %, or 40-50 wt. % of the lubricating composition. Example lubricating compositions include 5-30 wt. %, or 5-20 wt. %, or 5-15 wt. %, or 5-10 wt. %, or 20-40 wt. % of the exemplary copolymer.

[0098] A ratio of the weight of the oil of lubricating viscosity to the weight of the exemplary copolymer in the lubricating composition may be from 5:95 to 95:5, or from 40:60 to 80:20. A ratio of the weight of the exemplary copolymer to the weight of the dispersants in the lubricating composition may be from 98:2 to 100:0, or from 99:1 to 100:0, or from 99.5:0.5 to 100:0.

[0099] In some embodiments, a lubricant concentrate may be admixed with a base oil to form the lubricating composition. The lubricant concentrate may be formulated as for the lubricating composition but may include the oil of lubricating viscosity in a lesser amount than in the fully formulated lubricating composition or may contain no oil of lubricating viscosity. The lubricant concentrate may be combined with additional oil to form, in whole or in part, a finished lubricant, and thus the ratio of the copolymer to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or from 80:20 to 10:90 by weight.

[0100] The lubricating composition may include one or more additives in addition to the exemplary copolymer and oil of lubricating viscosity, such as one or more performance additives, such as other viscosity index improvers, extreme pressure agents, antiwear agents, antiscuffing agents, corrosion inhibitors, and the like.

A. Oil of Lubricating Viscosity

[0101] Suitable oils of lubricating viscosity include natural and synthetic oils, oils derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils, and mixtures thereof.

[0102] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0103] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0104] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0105] Natural oils useful as oils of lubricating viscosity include animal oils or vegetable oils (e.g., castor oil or lard oil), mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types, and oils derived from coal or shale or mixtures thereof.

[0106] Synthetic lubricating oils useful as oils of lubricating viscosity include hydrocarbon oils, such as polymerized and copolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof, and mixtures thereof.

[0107] Other synthetic lubricating oils include polyol esters (such as Priolube® 3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane

phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment, oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid (GTL) oils.

[0108] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulfur content >0.03 wt. %, and/or <90 wt. % saturates, viscosity index 80-120); Group II (sulfur content ≤ 0.03 wt. %, and ≥ 90 wt. % saturates, viscosity index 80-120); Group III (sulfur content ≤ 0.03 wt. %, and ≥ 90 wt. % saturates, viscosity index ≥ 120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The exemplary oil of lubricating viscosity includes an API Group I, Group II, Group III, Group IV, Group V oil, or mixtures thereof. In some embodiments, the oil of lubricating viscosity is an API Group I, Group II, Group III, or Group IV oil, or mixtures thereof. In some embodiments, the oil of lubricating viscosity is an API Group I, Group II, or Group III oil, or mixtures thereof.

B. Performance Additives

[0109] The lubricating composition described herein optionally further includes one or more performance additives. The performance additives, other than the exemplary copolymer, may include at least one of metal deactivators, detergents, dispersants (but only in minor amounts), viscosity index improvers, friction modifiers, corrosion inhibitors, antiwear agents, extreme pressure agents, antiscuffing agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and mixtures thereof. Typically, the fully-formulated lubricating composition (or "oil") will contain one or more of these performance additives. Suitable amounts of these additives in the exemplary lubricating composition are given below. These amounts are all expressed on an oil-free basis, i.e., exclusive of any diluent.

1. Dispersants

[0110] As noted above, the exemplary fully-formulated lubricating composition is free or substantially free of dispersants for dispersing oxidation products, other than the exemplary esterified copolymer. Examples of dispersants which may be totally absent from the lubricating composition, or present in only limited amounts, as specified above, are given below.

[0111] Exemplary dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant and polymeric dispersants. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include succinimides, phosphonates, and combinations thereof.

[0112] Exemplary succinimides include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include poly(C3-C6 alkylene) succinimides, such as polyisobutylene succinimides, with a number average molecular weight of the polyisobutylene substituent in the range of 350 to 5000, or 500 to 3000, or 1000-2500, or from 1300 to 2500.

[0113] Exemplary conventional and high vinylidene polyisobutylenes which may be used in forming the succinimide dispersant are disclosed, for example, in U.S. Patent Nos. 3,215,707; 3,231,587; 3,515,669; 3,579,450; 3,912,764; 4,605,808; 4,152,499; 5,071,919; 5,137,980; 5,286,823; 5,254,649

[0114] Ethylene/alpha olefin copolymers which may be used in forming the succinimide dispersant are disclosed, for example, in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929; and 6,030,930.

[0115] Other exemplary dispersants can be derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc.

[0116] Another class of ashless dispersant is acylated polyalkylene polyamines of the type described in U.S. Patent No. 5,330,667.

[0117] Another class of ashless dispersants is Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially

formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0118] Various methods for the preparation of succinimide dispersants are known. For example the exemplary dispersant can be produced by reaction of a C3-C6 polyalkylene (e.g., polypropylene, polyisobutylene, polypentylene, polyheptylene) or derivative thereof (e.g., a chlorinated derivative) with a mono- or α,β unsaturated-dicarboxylic acid or anhydride thereof (such as maleic anhydride or succinic anhydride) to produce an acylated C3-C6 polyalkylene compound, which is reacted with an amine, such as a primary amine or a polyamine, such as a polyethylene amine, to produce the dispersant.

[0119] Some of the following references are directed toward making an acylated C3-C6 polyalkylene compound suited to use in forming succinimide dispersants while others disclose the making of a succinimide dispersant itself. Two step methods are described, for example, in U.S. Patent Nos. 3,087,936; 3,172,892; and 3,272,746; one step methods are described in U.S. Patent Nos. 3,215,707, 3,231,587; 3,912,764; 4,110,349; and 4,234,435; thermal methods for forming succinimides of tetraethylene pentamine are described in U.S. Patent Nos. 3,361,673 and 3,401,118; methods for forming succinimides of halogenated alpha-olefin polymers are described in U.S. Patent No. 5,266,223; free radical methods are described in U.S. Patent Nos. 4,505,834; 4,749,505, and 4,863,623; grafting methods are described in U.S. Patent Nos. 4,340,689; 4,670,515; 4,948,842 and 5,075,383.

[0120] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron compounds (such as boric acid), urea, thiourea, dimercaptotriazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. In one embodiment, the post-treated dispersant is borated.

[0121] While the exemplary lubricating composition may be dispersant-free, in one embodiment, to the extent that a dispersant is in fact present, only nitrogen-containing C3-C6 acylated polyalkylene compounds are used. In

particular, succinimide dispersants derived from the reaction of an acylated C3-C6 polyalkylene compound with an amine to form a succinic acid anhydride, are employed. It has been found that small amounts of such succinimide dispersants can be used without impacting the spot rating unduly. The exemplary copolymer, however, allows the amount of such dispersants to be minimized or avoided altogether, due to the advantageous effect of the copolymer on dispersion of oxidation products.

[0122] In one embodiment, the dispersant is present in the lubricating composition, e.g., at 0.01-2.5 wt. %, or at 0.01-2 wt. %, or at 0.01-1.75 wt. %, or at 0.01-1.5 wt. %, or at 0.5-2.5 wt. %, or at 0.5-1.75 wt. %, or at 0.5-1.5 wt. %, and consists essentially of a nitrogen-containing dispersant or dispersants derived from an acylated C3-C6 polyalkylene compound. By consists essentially of, it is meant that no more than 0.2 wt. %, or no more than 0.1 wt. %, no more than 0.01 wt. % of the lubricating composition is dispersants other than these. A gear oil produced with such low levels of dispersant is still highly effective due to the presence of the exemplary esterified copolymer.

[0123] In one embodiment, the exemplary copolymer is substantially free of nitrogen, as defined above, and the lubricating composition contains no more than 1.75 wt. % dispersant, other than the exemplary copolymer.

2. Detergents

[0124] The lubricating composition optionally further includes known neutral or overbased detergents, i.e., ones prepared by conventional processes known in the art. Suitable detergents include phenates, sulfur containing phenates, sulfonates, salixarates, salicylates, carboxylic acid, phosphorus acids, alkyl phenols, sulfur coupled alkyl phenol compounds, and saligenins. The detergent may be present at 0 wt. % to 1 wt. %, or 0.01 wt. % to 1 wt. %, or 0.05 wt. % to 0.75 wt. %, or 0.1 wt. % to 0.75 wt. % of the lubricating composition.

3. Antioxidants

[0125] Antioxidant compounds useful herein as oxidation inhibitors include sulfurized olefins, diphenylamines, phenyl-alpha-naphthylamines, hindered

phenols, molybdenum dithiocarbamates, and mixtures and derivatives thereof. Antioxidant compounds may be used alone or in combination.

[0126] Exemplary diphenylamines include diarylamines, such as alkylated diphenylamines.

[0127] Exemplary hindered phenol antioxidants may contain a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, and mixtures thereof. In one embodiment, the hindered phenol antioxidant is an ester and may include, e.g., Irganox™ L-135 from Ciba. Suitable examples of molybdenum dithiocarbamates which may be used as an antioxidant include commercial materials sold under the trade names Vanlube 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 and S-600 from Asahi Denka Kogyo K. K, and mixtures thereof.

[0128] The antioxidant(s) may be present at up to 2 wt. %, or up to 1.5 wt. %, or up to 1.0 wt. %, or up to 0.7 wt. % of the lubricating composition, such as at least 0.001 wt. %, or at least 0.01 wt. %, or at least 0.1 wt. % of the lubricating composition.

4. Viscosity index improvers

[0129] Viscosity index improvers, other than the exemplary copolymer, may include hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, polyalkyl styrenes, polyolefins, polyalkyl (meth)acrylates, and mixtures thereof. In one embodiment, the viscosity index improver (polymeric thickener) is a poly(meth)acrylate.

5. Antiwear Agents

[0130] The lubricating composition optionally further includes at least one antiwear agent.

[0131] Examples of suitable antiwear agents include oil soluble amine salts of phosphorus compounds, sulfurized olefins, metal dihydrocarbyldithiophosphates (such as zinc dialkyldithiophosphates), thiocarbamate-containing compounds, such as thiocarbamate esters, thiocarbamate amides, thiocarbamic ethers, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulfides.

[0132] In one embodiment, the oil soluble phosphorus amine salt antiwear agent includes an amine salt of a phosphorus acid ester or mixtures thereof. The amine salt of a phosphorus acid ester includes phosphoric acid esters and amine salts thereof; dialkyldithiophosphoric acid esters and amine salts thereof; amine salts of phosphites; and amine salts of phosphorus-containing carboxylic esters, ethers, and amides; and mixtures thereof. The amine salt of a phosphorus acid ester may be used alone or in combination.

[0133] In one embodiment, the oil soluble phosphorus amine salt includes partial amine salt-partial metal salt compounds or mixtures thereof. In one embodiment, the phosphorus compound further includes a sulfur atom in the molecule. In one embodiment, the amine salt of the phosphorus compound is ashless, i.e., metal-free (prior to being mixed with other components).

[0134] The amines which may be suitable for use as the amine salt include primary amines, secondary amines, tertiary amines, and mixtures thereof. The amines include those with at least one hydrocarbyl group, or, in certain embodiments, two or three hydrocarbyl groups. The hydrocarbyl groups may contain 2 to 30 carbon atoms, or in other embodiments 8 to 26, or 10 to 20, or 13 to 19 carbon atoms.

[0135] Primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleylamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0136] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine and morpholine.

[0137] The amine may also be a tertiary-aliphatic primary amine. The aliphatic group in this case may be an alkyl group containing 2 to 30, or 6 to 26, or 8 to 24 carbon atoms. Tertiary alkyl amines include monoamines such as tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

[0138] In one embodiment, the phosphorus acid amine salt includes an amine with C₁₁ to C₁₄ tertiary alkyl primary groups or mixtures thereof. In one embodiment, the phosphorus acid amine salt includes an amine with C₁₄ to C₁₈ tertiary alkyl primary amines or mixtures thereof. In one embodiment, the phosphorus acid amine salt includes an amine with C₁₈ to C₂₂ tertiary alkyl primary amines or mixtures thereof.

[0139] Mixtures of amines may also be used herein. In one embodiment a useful mixture of amines is "Primene® 81R" and "Primene® JMT." Primene® 81R and Primene® JMT (both produced and sold by Rohm & Haas) are mixtures of C₁₁ to C₁₄ tertiary alkyl primary amines and C₁₈ to C₂₂ tertiary alkyl primary amines respectively.

[0140] In one embodiment, oil soluble amine salts of phosphorus compounds include a sulfur-free amine salt of a phosphorus-containing compound which is obtained/obtainable by a process comprising: reacting an amine with either (i) a hydroxy-substituted di-ester of phosphoric acid, or (ii) a phosphorylated hydroxy-substituted di- or tri- ester of phosphoric acid. A more detailed description of compounds of this type is disclosed in US Pub. No. 2008/0182770.

[0141] In one embodiment, the hydrocarbyl amine salt of an alkylphosphoric acid ester is the reaction product of a C₁₄ to C₁₈ alkylated phosphoric acid with the Primene 81R™ product (produced and sold by Rohm & Haas) which is a mixture of C₁₁ to C₁₄ tertiary alkyl primary amines.

[0142] Examples of hydrocarbyl amine salts of dialkyldithiophosphoric acid esters include the reaction product(s) of isopropyl, methyl-amyl (4-methyl-2-pentyl or mixtures thereof), 2-ethylhexyl, heptyl, octyl or nonyl dithiophosphoric acids with ethylene diamine, morpholine, or Primene 81R™, and mixtures thereof.

[0143] In one embodiment, the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product is further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide includes an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, and styrene oxide. In one embodiment, the epoxide is propylene oxide. The glycols may be aliphatic glycols having from 1 to 12, or from 2 to 6, or 2 to 3 carbon atoms. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of forming the same are described in U.S. Patent Nos. 3,197,405 and 3,544,465. The resulting acids may then be salted with amines. An example of suitable dithiophosphoric acid is prepared by adding phosphorus pentoxide (about 64 grams) at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and an acid number of 87 (bromophenol blue).

[0144] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally, the reaction occurs at a temperature from 25°C to 125°C.

[0145] Examples of suitable olefins that may be sulfurized to form the sulfurized olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene,

nonodecene, eicosene, and mixtures thereof. Hexadecene, heptadecene, octadecene, nonodecene, eicosene, and mixtures thereof, and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as butyl acrylate.

[0146] Another class of sulfurized olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil; and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid, and mixtures thereof. The fatty acids may be obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil, and mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins.

[0147] In an alternative embodiment, the ashless antiwear agent may be a monoester of a polyol and an aliphatic carboxylic acid, often an acid containing 12 to 24 carbon atoms. Often the monoester of a polyol and an aliphatic carboxylic acid is in the form of a mixture with a sunflower oil or the like, which may be present in the friction modifier mixture from 5 to 95, in several embodiments from 10 to 90, or from 20 to 85, or 20 to 80 weight percent of the mixture. The aliphatic carboxylic acids (especially a monocarboxylic acid) which form the esters are those acids typically containing 12 to 24, or from 14 to 20 carbon atoms. Examples of carboxylic acids include dodecanoic acid, stearic acid, lauric acid, behenic acid, and oleic acid.

[0148] Polyols include diols, triols, and alcohols with higher numbers of alcoholic OH groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabitol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. The polyol can be diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol, dipentaerythritol, or mixtures thereof.

[0149] The commercially available monoester known as "glycerol monooleate" is believed to include 60 ± 5 percent by weight of glycerol

monooleate, 35 ± 5 percent glycerol dioleate, and less than 5 percent trioleate and oleic acid. The amounts of the monoesters, described above, are calculated based on the actual, corrected, amount of polyol monoester present in any such mixture.

[0150] The antiwear agent(s) may be present at from 0.0 % wt. to 5 wt. %, or 0.5 % wt. to 5 wt. %, or 0.5 wt. % to 3 wt. %, or 1 wt. % to 2 wt. % of the lubricating composition.

6. Antiscuffing Agents

[0151] The lubricating composition may also contain an antiscuffing agent. Antiscuffing agent compounds are believed to decrease adhesive wear and are often sulfur containing compounds. Typically, the sulfur containing compounds include sulfurized olefins, organic sulfides and polysulfides, such as dibenzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, di-tertiary butyl polysulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, sulfurized terpene, sulfurized Diels-Alder adducts, alkyl sulphenyl N'N-dialkyl dithiocarbamates, the reaction product of polyamines with polybasic acid esters, chlorobutyl esters of 2,3-dibromopropoxyisobutyric acid, acetoxymethyl esters of dialkyl dithiocarbamic acid and acyloxyalkyl ethers of xanthogenic acids, and mixtures thereof.

[0152] The antiscuffing agent(s) may be present at from 0 % wt. to 6 wt. %, or 1 wt. % to 6 wt. %, or 3 wt. % to 6 wt. % of the lubricating composition.

7. Extreme Pressure Agents

[0153] Extreme Pressure (EP) agents that are soluble in the oil include sulfur- and chlorosulfur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; sulfurized olefins (such as sulfurized isobutylene), organic sulfides and polysulfides such as dibenzyl disulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, dimercaptotriazoles, sulfurized dipentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons such as the reaction product of phosphorus sulfide with turpentine or methyl oleate; phosphorus

esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids or derivatives including, for example, the amine salt of a reaction product of a dialkyldithiophosphoric acid with propylene oxide and subsequently followed by a further reaction with P_2O_5 ; and mixtures thereof (as described, for example, in U.S. Patent No. 3,197,405).

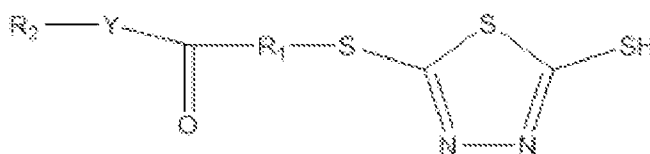
[0154] Suitable dimercaptothiadiazaoles include hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazaole and unsubstituted equivalents thereof that are substantially soluble at 25°C in non-polar media such as an oil of lubricating viscosity. The total number of carbon atoms in the hydrocarbyl-substituents, which tend to promote solubility, will generally be 8 or more, or 10 or more, or at least 12. If the thiadiazaole has two or more hydrocarbyl groups, the number of carbon atoms per group may be below 8 provided the total number of carbons is 8 or more.

[0155] Examples of dimercaptothiadiazaoles include 2,5-(tert-octyldithio)-1,3,4-thiadiazaole 2,5-(tert-nonyldithio)-1,3,4-thiadiazaole, 2,5-(tert-decyldithio)-1,3,4-thiadiazaole, 2,5-(tert-undecyldithio)-1,3,4-thiadiazaole, 2,5- (tert-dodecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-tridecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-tetradecyldithio)-1,3,4-thiadiazaole, 2,5- (tert-pentadecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-hexadecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-heptadecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-octadecyldithio)-1,3,4-thiadiazaole, 2,5-(tert-nonadecyldithio)-1,3,4-thiadiazaole or 2,5-(tert-eicosyldithio)-1,3,4-thiadiazaole, and oligomers and mixtures thereof. In one embodiment, the dimercaptothiadiazaole includes 2,5-dimercapto-1,3,4-thiadiazaole.

[0156] Dimercaptothiadiazaoles may be derived from 2,5-dimercapto-1,3,4-thiadiazaole, or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazaole, or an oligomer thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazaole typically form by forming a sulfur-sulfur bond between 2,5-dimercapto-1,3,4-thiadiazaole units to form oligomers of

two or more of the thiadiazole units. In one embodiment the dimercaptothiadiazole (typically a 2,5-dimercapto-1,3,4-thiadiazole) may be formed by reacting a dimercaptothiadiazole with an ethylenically unsaturated amide or ester. The amide or ester may include hydrocarbyl-(meth)acrylate or hydrocarbyl-(meth)acrylamide, a hydrocarbyl-substituted maleate, a hydrocarbyl-substituted crotonate, a hydrocarbyl-substituted cinnamate, or mixtures thereof.

[0157] In one embodiment, the dimercaptothiadiazole (typically a 2,5-dimercapto-1,3,4-thiadiazole) may be a compound represented by the formula:



where:

R₁ may be an alkylene group containing 1 to 5, or 1 to 3, or 2 carbon atoms;

R₂ may be a hydrocarbyl group containing 1 to 16, or 2 to 8, or 4 carbon atoms;

Y may be -O- or >NR₃ (typically Y may be -O-); and

R₃ may be hydrogen or R₂.

[0158] The dimercaptothiadiazole of the formula above may be prepared by reacting the appropriate hydrocarbyl-(meth)acrylate or hydrocarbyl-(meth)acrylamide with 2,5-dimercapto-1,3,4-thiadiazole. The reaction of hydrocarbyl-(meth)acrylate or hydrocarbyl-(meth)acrylamide with 2,5-dimercapto-1,3,4-thiadiazole may be carried out at a temperature in the range of 50°C to 150°C, or 70°C to 120°C, or 80°C to 100°C.

[0159] In one embodiment, the dimercaptothiadiazole salt (typically a 2,5-dimercapto-1,3,4-thiadiazole salt) may be prepared by reacting a dimercaptothiadiazole with an epoxide.

[0160] The EP agents may be present at from 0 % wt. to 6 wt. %, or 1 % wt. to 6 wt. %, or 2 wt. % to 6 wt. %, or 3 wt. % to 6 wt. % of the lubricating composition.

8. Corrosion Inhibitors, Foam Inhibitors, Pour Point
Depressants, Friction Modifiers

[0161] Corrosion inhibitors that may be useful include fatty amines, octylamine octanoate, and condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine.

[0162] The corrosion inhibitor(s) may be present at 0 wt. % to 3 wt. %, or 0.01 % wt. to 3 wt. %, or 0.01 to 1 wt. %, or 0.05 to 0.5 wt. % of the lubricating composition.

[0163] Foam inhibitors that may be useful in the exemplary compositions include silicones; copolymers of ethyl acrylate and 2-ethylhexylacrylate, which can optionally further include vinyl acetate; and demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0164] Pour point depressants that may be useful in the exemplary compositions include polyalphaolefins, esters of maleic anhydride-styrene copolymers, and poly(meth)acrylates, polyacrylates, and polyacrylamides, such as polyalkylmethacrylates.

[0165] Friction modifiers that may be useful in the exemplary compositions include fatty acid derivatives such as amines, esters, epoxides, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids.

[0166] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, long chain fatty esters, or derivatives of long chain fatty epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; fatty alkyl tartramides; fatty glycolates; fatty glycolamides fatty phosphonates; fatty phosphites; borated phospholipids, borated fatty epoxides; glycerol esters; borated glycerol esters; fatty amines; alkoxylated fatty amines; borated alkoxylated fatty amines; hydroxyl and polyhydroxy fatty amines including tertiary hydroxy fatty amines; hydroxy alkyl amides; metal salts of fatty acids; metal salts of alkyl salicylates; fatty oxazolines; fatty ethoxylated alcohols; condensation products of carboxylic acids and

polyalkylene polyamines; or reaction products from fatty carboxylic acids with guanidine, aminoguanidine, urea, or thiourea and salts thereof. As used herein the term “fatty alkyl or fatty” in relation to friction modifiers means a carbon chain having 10 to 22 carbon atoms, typically a straight carbon chain. Friction modifiers may also encompass materials such as sulfurized fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, and monoesters of a polyol and an aliphatic carboxylic acid derived or derivable from sunflower oil or soybean oil.

[0167] In one embodiment, the friction modifier may be a long chain fatty acid ester. In another embodiment, the long chain fatty acid ester may be a mono-ester and in another embodiment the long chain fatty acid ester may be a (tri)glyceride.

[0168] The friction modifier may be present at 0 wt. % to 7 wt. %, or 0.1 wt. % to 6 wt. %, or 0.25 wt. % to 3.5 wt. %, or 0.5 wt. % to 2.5 wt. %, or 1 wt. % to 2.5 wt. %, or 0.05 wt. % to 0.5 wt. %, or 5 to 7 wt. % of the lubricating composition.

[0169] To the extent that any of the performance additives, other than dispersants, employed in the lubricating composition also act as dispersants of the products of oxidation, they may be avoided or minimized, as discussed for the dispersants above, such that the total of all dispersants is no more than 2 wt. %, or no more than 1.5 wt. %, or no more than 1 wt. %, or no more than 0.5 wt. %, or no more than 0.2 wt. %.

III. Industrial Application

[0170] The method and exemplary lubricating composition may be suitable for refrigeration lubricants, greases, gear oils, axle oils, drive shaft oils, traction oils, manual transmission oils, automatic transmission oils, metal working fluids, hydraulic oils, or internal combustion engine oils. The exemplary lubricating composition may be supplied to a mechanical device, such as a gear or transmission system, without addition of any further dispersants, and used for lubrication during normal operation of the mechanical device.

[0171] In one embodiment, the method and exemplary lubricating composition may be suitable for at least one of gear oils, axle oils, drive shaft oils, traction oils, manual transmission oils and automatic transmission oils.

[0172] As an example, the exemplary lubricating composition finds application as a gear oil.

[0173] The exemplary copolymer may also find application in automatic transmission systems, such as continuously variable transmissions (CVT), infinitely variable transmissions (IVT), toroidal transmissions, continuously slipping torque converter clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

[0174] The use (may also be referred to as a method) and lubricating composition described herein are capable of providing a lubricant with acceptable/improved dispersancy properties (cleanliness) and oxidation control, and may also provide one (or at least two, or all) of acceptable or improved shear stability, acceptable or improved viscosity index control, and acceptable or improved low temperature viscosity.

[0175] In several embodiments, a suitable lubricating composition includes the copolymer present (on an active basis) in ranges as shown Table I.

TABLE 1

	Embodiments (wt. % of lubricating composition)		
	A	B	C
Exemplary copolymer	5-95	30-60	40-50
Other Performance Additives	0-20	0.5-20	0.5-15
Oil of Lubricating Viscosity	0.01-95	20-69.5	35-59.5
Total of three components	100	100	100

[0176] Unexpectedly, the exemplary copolymer-containing fluids were found to disperse the byproducts of oxidation without the use of additional dispersant. The lubricating composition was shown to improve in this respect as dispersant is reduced or removed.

[0177] The following examples provide an illustration of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

Example 1: Preparation of an amine-capped esterified copolymer (Copolymer 1)

[0178] A 5L reaction flask was charged with 407.8 g of maleic anhydride (MAA), 700 g of 1-dodecene and 1108 g of toluene. A molar ratio of the 1-dodecene:maleic anhydride was 1:1. The flask was fitted with a PTFE gasket and a 5-port flange lid equipped with an overhead stirrer, stirrer guide, thermocouple, nitrogen inlet (250 cm³/min nitrogen), silicon septa with peristaltic pump attached via cannula and a water condenser. The reaction flask and its contents were heated to 108°C

[0179] A mixture of 35.98 grams of Trigonox®21S (a commercially available tert-butyl peroxy-2-ethylhexanoate initiator from Akzo Nobel), 26.94g of n-dodecylmercaptan, and 485 g of toluene were mixed together and added to the reaction flask over 240 min. via the peristaltic pump. The reaction mixture was stirred at 108°C for several hours. The reaction flask was fitted with a Dean-Stark trap and the reaction mixture heated to 120°C with stirring. Using the peristaltic pump, 618.1g of Alfol 810™ was added over 45 min. and the resulting reaction mixture stirred for 1 hr. An additional 618g of Alfol 810™ and 28.55g of a 70% aqueous solution of methane sulfonic acid were added to the reaction flask over 3 to 4 hrs while gradually increasing the reaction temperature to 135°C. The reaction mixture was then heated to 145°C and 70g of n-butanol and 14.27g of 70% aqueous solution of methane sulfonic acid were added and stirred for 1 hour. An additional 70g of n-butanol was added and the reaction stirred for 2 hours. The addition of n-butanol was continued until the 1-dodecene:maleic anhydride copolymer was esterified to at least 97%. Sufficient sodium hydroxide (50% aqueous sodium hydroxide solution) was added to quench the methane sulfonic acid and the mixture was stirred for 1 hour followed by the addition of 47.98g of 4-(3-aminopropyl)morpholine and stirred for an additional 2 hours. The reaction flask was fitted for vacuum stripping and the resultant product vacuum-stripped (-28 in Hg) at 150°C and held for 2.5 hours. The vacuum was removed and the flask was cooled to 120°C. The resulting reaction mixture was filtered using fax-5 and filter cloth.

[0180] Product analysis showed a 0.103 wt. % nitrogen content, a kinematic viscosity at 100°C (KV100), determined employing ASTM method D445, was 288 cSt., and TAN was 4.5mg KOH/g. TAN is the total acid number, determined by 0.1M KOH titration with phenolphthalein indicator in toluene/isopropanol/water (500:495:5 parts), measured in mg KOH/g.

[0181] GPC run in tetrahydrofuran against polystyrene standards showed a M_w of 16,400, M_n of 7900, and a PDI (M_w/M_n) of 2.06 for the esterified, amine-capped copolymer.

Example 2: Preparation of an amine-capped esterified copolymer
(Copolymer 2)

[0182] The same procedure used in Example 1 was followed except that the copolymer of 1-dodecene:maleic anhydride made in Example 1 was esterified with a mixture of 84.4 weight % Alfol 810TM and 15.6 weight % Isofol 16TM and amine end capping of the esterified copolymer was performed with n-butylamine.

[0183] Product analysis showed a 0.23 wt. % nitrogen content, a kinematic viscosity at 100°C (KV100), determined employing ASTM method D445, of 390 cSt., and TAN was 3.3 mg KOH/g.

[0184] GPC run in tetrahydrofuran against polystyrene standards showed a M_w of 16,448, M_n of 7,300, and a PDI of 2.25 for the esterified, amine-capped copolymer.

Example 3: Preparation of an esterified copolymer without amine
cap (Copolymer 3)

[0185] A similar procedure to that used in Example 1 was followed except that the copolymer of 1-dodecene:maleic anhydride made in Example 1 was esterified with a mixture of Alfol 810TM and Isofol 16TM in a 9:1 weight % ratio. Following the esterification with Alfol 810TM and Isofol 16TM, the esterification of the copolymer was finished with n-butanol, as described in Example 1. No amine end capping of the esterified copolymer was performed.

[0186] Product analysis showed a 100°C (KV100), determined with ASTM method D445, was 248 cSt. and TAN was 6.3 mg KOH/g.

[0187] GPC run in tetrahydrofuran against polystyrene standards showed a M_w of 13,177, M_n of 6549, and a PDI of 2.01 for the esterified copolymer.

Example 4: Preparation of an amine-capped esterified copolymer (Copolymer 4)

[0188] A similar procedure to that used in Example 1 was followed except that the copolymer of 1-dodecene:maleic anhydride made in Example 1 was esterified with a mixture of Alfol 810™ and Isofol 16™ in a 9:1 weight % ratio. Following the esterification with Alfol 810™ and Isofol 16™, the esterification of the copolymer was finished with n-butanol as described in Example 1, and amine end capping of the esterified copolymer was performed with aminoethylethyleneurea.

[0189] Product analysis showed a 0.14 wt. % nitrogen content, a kinematic viscosity at 100°C (KV100), determined with ASTM method D445, of 211.3 cSt., and TAN was 3.3 mg KOH/g.

Example 5: Preparation of Lubricating Compositions

[0190] The amine-capped esterified copolymer (Copolymer 2) prepared according to Example 2 was used to prepare lubricating compositions A, B, and C (COMP. A, COMP. B, and COMP. C) as shown in TABLE 2. All amounts are in wt. %. The components of the performance package (dispersant-free) are given in TABLE 3 and are expressed on an oil free basis. Compositions D, E, and F (COMP. D, COMP. E and COMP. F respectively) were prepared with esterified only copolymer (Copolymer 3) prepared according to Example 3. All amounts are in wt. %.

[0191] It is to be noted that the actual amounts of dispersant in the composition are only 67% of those shown in TABLE 2 since the dispersant is diluted with 33 wt. % mineral oil. Thus, the maximum amount of dispersant used in these experiments was approximately 1.5 wt. %

TABLE 2

	COMP A	COMP B	COMP C	COMP D		COMP E	COMP F
				Run 1	Run 2		
Example 2 copolymer	40.48	41.43	41.43				
Example 3 copolymer				45.0	46.5	46.5	46.5
Dispersant (borated polyisobutylene succinimide) 33% mineral oil	2.25	1.125	0.225	2.25	2.25	1.125	0
Base Oil 1-Group III Base oil, Visc. @100°C~4 cSt)	36.99	37.121	37.796	38.17	32.47	33.32	34.16
Synthetic aliphatic hydrocarbon	12.33	12.374	12.599	11.2	10.825	11.106	11.387
Pour point depressant (polyalkylmethacrylate) 50% mineral oil	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Performance Package	7.75	7.75	7.75	7.75	7.75	7.75	7.75

TABLE 3

<u>wt. % present</u>	<u>Description</u>	<u>Function</u>
22.7	Phosphoric acid esters/amine salt	Antiwear
41.0	Olefin sulfide	Extreme pressure agent
19.6	Sulfurized isobutylene	Extreme pressure agent
0.12	Alkenyl amide	Friction modifier
5.07	Antifoam agents and Corrosion inhibitors	Antifoam agents and Corrosion inhibitors
Balance	Diluent Oil (Group III, 4 cSt)	

Oxidative Stability Testing

[0192] Compositions A, B, C, and D were oxidized using the CEC L-48-00 procedure B (whereby air is passed through 100ml of oil at a rate of 5 liters/hour for 192 hours at 160 °C). The results are shown in TABLE 4, expressed as the percentage increase in kinematic viscosity at 40°C (%KV40), and at 100°C (%KV100). The test procedure also measures a tube rating, and the dispersancy rating was calculated (as described above). For the spot rating, higher values indicate better results.

[0193] The kinematic viscosity is determined according to ASTM method D445 at 100°C (KV100) and at 40°C (KV40).

[0194] The viscosity index (VI) is determined according to ASTM method D2270.

TABLE 4

	COMP. A	COMP. B	COMP. C	COMP. D		COMP. E	COMP. F
				Run 1	Run 2		
CEC_TUBE RATING	3	3	3	2	2	3	3
SPOT RATING	30	46	79	66	74	25	38
%KV40 %	109.7	115.6	105	212.5	173	77	54
%KV100 %	91	95.2	85	181.3	149	64	43.8
TAN_CHANGE mg KOH/g	2.4	3.1	2.4	7.7			
¹ KV40, cSt	103.28	101.79	97.52	114.8	125.4	118.2	111.3
¹ KV100, cSt	18.14	18.02	17.53	18.75	20.39	19.51	18.69
¹ VI	195	196	198	184	187	188	188

¹Viscosity at start of test.

[0195] The DKA results of COMP. A, COMP. B and COMP. C show that as the dispersant concentration is decreased, a higher dispersant spot rating at equal tube rating at approximately equal viscosity increase is achieved. While the DKA results of COMP. D indicate higher oxidation of the oil (i.e., higher TAN change and higher KV100), the spot rating indicates that the oxidation products are still dispersed by the exemplary copolymer, Copolymer 3 (Example 3) despite the copolymer not having been amine capped.

Example 6: Comparison with Lubricating Compositions Containing Other Viscosity Index Improvers

[0196] Lubricating compositions containing other viscosity index improvers were investigated to determine whether they would also show this unexpected result. The compositions tested are shown in TABLE 5. The Exemplary copolymers, Copolymer 1 (Example 1) and Copolymer 4 (Example 4), were used to form Compositions G, H, and J (Example 1) and

Compositions K, L and M (Example 4). Polyalphaolefin (PAO 100), a Group IV base oil, was used to form Comparative Compositions N, O, and P, and poly(alkyl methacrylate) (PMA) was used in the preparation of Comparative Compositions Q, and R. The dispersant, where used, was a borated polyisobutylene succinimide dispersant. The same performance package disclosed in TABLE 3 was used. The results are shown in TABLE 6.

TABLE 5: Lubricating Compositions

Lubricating Composition	G	H	J	K	L	M
Dispersant (33% mineral oil)	2.25	1.125	0	2.25	1.125	0
Base Oil 3-Group III Base oil, Visc. @100°C~4 cSt	33.3	33.17	32.97	32.47	33.32	34.16
Synthetic aliphatic hydrocarbon	11.1	11.05	10.98	10.82	11.11	11.39
PMA 22% mineral oil						
PAO 100						
Copolymer 1	45.4	46.7	48.1			
Copolymer 4				45.6	45.6	45.6
Pour point depressant (polyalkylmethacrylate) 50% mineral oil	0.2	0.2	0.2	0.2	0.2	0.2
Performance package	7.75	7.75	7.75	7.75	7.75	7.75
Lubricating Composition	N	O	P	Q	R	N
Dispersant (33% mineral oil)	2.25	1.125	0	2.25	0	2.25
Base Oil 3-Group III Base oil, Visc. @100°C~4 cSt	35.7	35.57	35.44	36.98	36.87	35.7
Synthetic aliphatic hydrocarbon	11.9	11.85	11.81	12.32	12.28	11.9
PMA 22% mineral oil				40.5	42.9	
PAO 100	42.2	43.5	44.8			42.2
Copolymer 1						
Copolymer 4						
Pour point depressant (polyalkylmethacrylate) 50% mineral oil	0.2	0.2	0.2	0.2	0.2	0.2
Performance package	7.75	7.75	7.75	7.75	7.75	7.75

TABLE 6: DKA Performance of Lubricating Compositions

Lubricating Composition	G	H	J	K	L	M
OXIDATION, DKA						
CEC_TUBE RATING	3	3	3	2	2	3
SPOT RATING	91	93	100	100	100	41
%KV40	176.3	108.3	109.4	206	118.4	109.1
%KV100	142.4	87.4	87.3	163.4	97.5	87.5
TAN CHANGE mg KOH/g	12	3.7	5.1			
KV40, cSt	109.2	106.4	106.9	122.3	115.9	108.9
KV100, cSt	18.19	17.96	18.12	19.68	18.95	18.05
VI	186	187	189	184	184	184

Lubricating Composition	N	O	P	Q	R
OXIDATION, DKA					
CEC_TUBE RATING	3	3	3	3	3
SPOT RATING	23	35	49	91	92
%KV40	166.1	28.7	29.1	214.9	198.3
%KV100	128.2	24	23.9	145.4	145.3
TAN CHANGE mg KOH/g	7	0	-0.1	9.2	6.1
KV40, cSt	129.9	131	132.6	121.8	123.9
KV100, cSt	18.78	18.91	19.14	18.72	19.02
VI	163	163	164	173	174

[0197] The results show that a change in dispersant level provides no change in dispersancy for the PMA bulk fluid, as demonstrated by the spot rating. PAO100 shows a modest improvement in spot rating but the results are still significantly lower (i.e., not acceptable for some applications) than spot ratings achieved using the exemplary copolymers. The exemplary Copolymer 1 shows an improvement in spot rating and viscosity increase at equivalent CEC tube rating (3). The results suggest that the exemplary

copolymer is capable of fully dispersing the products of oxidation without the addition of further dispersants. The results also indicate that PAO100 cannot achieve this, with or without dispersant, and that PMA has a more substantial viscosity increase, tube rating and incomplete dispersancy under the same conditions.

[0198] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0199] As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration. As used herein any member of a genus (or list) may be excluded from the claims.

[0200] As used herein, the term "(meth) acrylic" and related terms includes both acrylic and methacrylic groups.

[0201] As used herein, the term "a primary alcohol branched at the β - or higher position" relates to an alcohol with branching at the 2- position or a higher position (e.g., 3-, or 4-, or 5-, or 6-, or 7- position, etc.).

[0202] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to

the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

a. hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

b. substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

c. hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms; and

d. heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, in one aspect no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0203] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

[0204] It will be appreciated that variants of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims.

WHAT IS CLAIMED IS:

1. A lubricating composition comprising:
 - a) an esterified copolymer with a backbone comprising units derived from a vinyl aliphatic monomer and units derived from a carboxylic acid monomer, the carboxylic acid monomer comprising an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof;
 - b) an oil of lubricating viscosity; andwherein the lubricating composition comprises no more than 2.5 wt. % of dispersant for dispersing oxidation products, other than the esterified copolymer.
2. The lubricating composition of claim 1, wherein the lubricating composition comprises no more than 2 wt. %, or no more than 1.75 wt. %, or no more than 1.5 wt. %, or no more than 1 wt. %, or no more than 0.5 wt. %, or no more than 0.2 wt. % or no more than 0.1 wt. % dispersant, other than the exemplary copolymer.
3. The lubricating composition of claim 1 or 2, wherein the lubricating composition comprises dispersant, other than the exemplary copolymer, at 0.01-2.5 wt. %, or at 0.01-2 wt. %, or at 0.01-1.75 wt. %, or at 0.01-1.5 wt. %, or at 0.5-2.5 wt. %, or at 0.5-1.75 wt. %, or at 0.5-1.5 wt. %.
4. The lubricating composition of any one of claims 1 to 3, wherein the dispersant is present and consists essentially of a nitrogen-containing dispersant derived from an acylated C3-C6 polyalkylene compound.
5. The lubricating composition of any one of claims 1 to 4, wherein the esterified copolymer comprises a nitrogen-containing group.
6. The lubricating composition of any one of claims 1 to 5, wherein at least some of the units derived from the carboxylic acid monomer are at least one of aminated, amidated, and imidated with a nitrogen-containing compound.

7. The lubricating composition of claim 6, wherein the nitrogen-containing compound is an amine-containing compound selected from the group consisting of morpholines, imidazolidinones, amino amides, β -alanine alkyl esters, aliphatic amines, aromatic amines, aliphatic polyamines, aromatic polyamines, and mixtures thereof.
8. The lubricating composition of claim 6 or 7, wherein 0.1 to 25 % of carboxylic acid functionalities of the units derived from the carboxylic acid monomer are at least one of aminated, amidated, and imidated with a nitrogen-containing compound.
9. The lubricating composition of any one of claims 6 to 8, wherein at least 1% of carboxylic acid functionalities on the units derived from the carboxylic acid monomer are reacted with a nitrogen-containing compound to provide a nitrogen-containing group.
10. The lubricating composition of any one of claims 1 to 3, wherein the esterified copolymer is substantially free of a nitrogen-containing group.
11. The lubricating composition of claim 10, wherein the lubricating composition comprises no more than 2 wt. % dispersant, other than the exemplary copolymer.
12. The lubricating composition of any one of claims 1 to 11, wherein the esterified copolymer has a weight average molecular weight of 5,000-25,000.
13. The lubricating composition of any one of claims 1 to 12, wherein the esterified copolymer has a weight average molecular weight of 5000 to 10,000, or 15,000-25,000, or 10,000 to 17,000.
14. The lubricating composition of any one of claims 1 to 13, wherein the esterified copolymer is at least 5 wt. % of the lubricating composition.

15. The lubricating composition of any one of claims 1 to 14, wherein the esterified copolymer is at least 10 wt. %, or at least 40 wt. %, or at least 60 wt. % of the lubricating composition.
16. The lubricating composition of any one of claims 1 to 15, wherein the esterified copolymer is 30-60 wt.%, or 40-50 wt. % of the lubricating composition.
17. The lubricating composition of any one of claims 1 to 16, wherein the oil of lubricating viscosity is at least 20 wt. %, or at least 30 wt. % of the lubricating composition.
18. The lubricating composition of any one of claims 1 to 17, wherein the copolymer is esterified with a primary alcohol.
19. The lubricating composition of claim 18, wherein the primary alcohol comprises a primary alcohol which is branched at the β - or higher position.
20. The lubricating composition of claim 18 or 19, wherein the primary alcohol further comprises a linear primary alcohol.
21. The lubricating composition of any one of claims 18 to 20, wherein the primary alcohol comprises at least 6 carbon atoms.
22. The lubricating composition of any one of claims 1 to 21, wherein the carboxylic acid monomer comprises maleic anhydride.
23. The lubricating composition of any one of claims 1 to 22, wherein the vinyl aliphatic monomer comprises an alpha-olefin.
24. The lubricating composition of claim 23, wherein the alpha-olefin comprises at least 6 carbon atoms.

25. The lubricating composition of any one of claims 1 to 24, wherein a molar ratio of the vinyl aliphatic monomer units to the carboxylic acid monomer units in the copolymer is from 1:3 to 3:1, or from 0.6:1 to 1.2:1, or from 0.7:1 to 1:1.1.
26. The lubricating composition of any one of claims 1 to 25, wherein the esterified copolymer backbone further comprises units derived from a vinyl aromatic monomer.
27. The lubricating composition of claim 26, wherein a molar ratio of the units derived from the vinyl aromatic monomer to the units derived from the vinyl aliphatic monomer is from 0:100 to 25:75, or up to 10:90.
28. The lubricating composition of any one of claims 1 to 27, wherein the copolymer backbone comprises at least 20 of the units, or at least 100 of the units.
29. The lubricating composition of any one of claims 1 to 28, wherein the copolymer backbone comprises up to 1000 of the units, or up to 500 of the units, or up to 250 of the units derived from the vinyl aliphatic monomer and the carboxylic acid monomer.
30. The lubricating composition of any one of claims 1 to 29, further comprising at least one performance additive, other than the esterified copolymer.
31. The lubricating composition of claim 30, wherein the at least one other performance additive comprises at least one of the group consisting of metal deactivators, detergents, viscosity index improvers, friction modifiers, corrosion inhibitors, antiwear agents, extreme pressure agents, antiscuffing agents, antioxidants, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, and mixtures thereof.

32. The lubricating composition of claim 31, wherein the at least one other performance additive comprises an extreme pressure agent selected from the group consisting of dimercapto-1,3,4-thiadiazole, derivatives of dimercapto-1,3,4-thiadiazole, sulfurized olefins, and mixtures thereof.

33. The lubricating composition of any one of claims 1 to 32, wherein the lubricating composition comprises, in total, less than 2 wt. %, or less than 1.75 wt. %, or less than 1.5 wt. %, or less than 1 wt. %, or less than 0.5 wt. %, or less than 0.2 wt. % of dispersants selected from the group consisting of N-substituted long chain alkenyl succinimides, polyisobutylene succinimide complexed with zinc, Mannich bases, and post-treated dispersants formed by borating these compounds.

34. The lubricating composition of any one of claims 1 to 33, wherein the 20hr KRL SSI of the lubricating composition is from 0-30, or from 0-10, or from 10-30.

35. A process for preparing a lubricating composition comprising:

(A) forming an esterified copolymer comprising:

(1) reacting (i) a vinyl aliphatic monomer and (ii) a carboxylic acid monomer comprising an α,β -ethylenically unsaturated dicarboxylic acid or derivative thereof, to form a copolymer, wherein the carboxylic acid monomer optionally has ester groups,

(2) optionally, esterifying the copolymer of step (1) to form an esterified copolymer, and

(3) optionally, reacting the copolymer of step (1) or (2) with an nitrogen-containing compound in an amount to provide an esterified copolymer with at least 0.01 wt. % nitrogen; and

wherein the resulting copolymer is esterified in at least one of (1), (2), and (3); and

(B) mixing the esterified copolymer formed in (A) with at least one of an oil of lubricating viscosity and a performance additive other than the esterified copolymer, to provide a lubricating composition comprising no more than 2.5 wt. % of dispersant, other than the esterified copolymer, for dispersing oxidation products.

36. The process of claim 35, comprising step (3).

37. The process of claim 35 or 36, wherein the reacting of the esterified copolymer of step (1) or (2) with an nitrogen-containing compound provides the esterified copolymer with 0.01 wt. % to 1.5 wt. %, or 0.02 wt. % to 0.75 wt. %, or 0.04 wt. % to 0.25 wt. % nitrogen.

38. The process of any one of claims 35 to 37, comprising step (2).

39. The process of any one of claims 35 to 38, wherein the carboxylic acid monomer has ester groups derived from a primary alcohol to provide an esterified copolymer in step (1).

40. A lubricating composition formed by the method of any one of claims 35 to 39.

41. The use of the lubricating composition of any one of claims 1 to 34 and 40 in a driveline system of an automotive vehicle without addition of any further dispersants.

42. A method for lubricating a component of a driveline system of a vehicle comprising supplying the lubricating composition of any one of claims 1 to 34 and 40 to the component.