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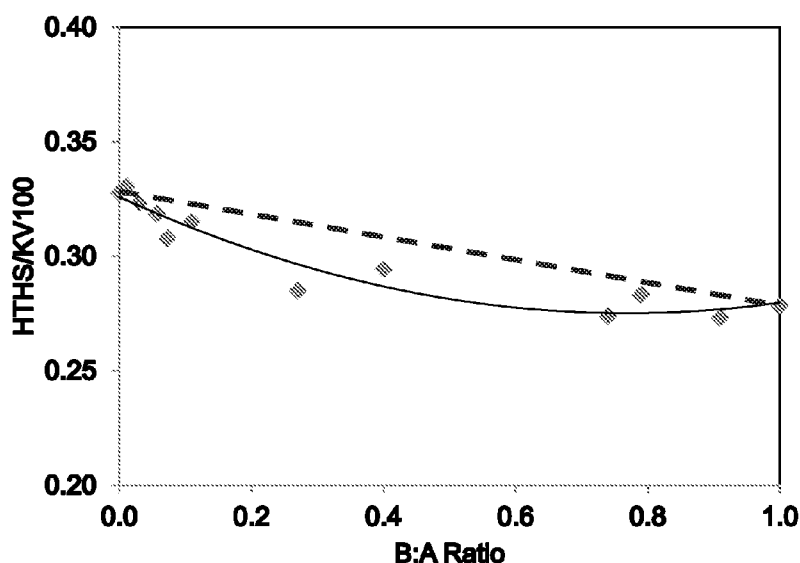
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(54) Title: LUBRICATING COMPOSITION INCLUDING ESTERIFIED COPOLYMER AND DIENE RUBBER POLYMER

Figure 1



(57) Abstract: A lubricating composition includes (A) an esterified copolymer comprising units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer, the vinyl monomer comprising a vinyl aliphatic monomer, the carboxylic acid monomer comprising an ethylenically unsaturated carboxylic acid or derivative thereof, esterified with a primary alcohol; and (B) a diene rubber copolymer comprising at least a first block (B1) derived from a conjugated diene monomer and at least a second block (B2) derived from a vinyl aromatic monomer. A ratio of the diene rubber copolymer to the esterified copolymer in the lubricating composition (B:A) is from 0.01 to 0.9, by weight.

3934-01**LUBRICATING COMPOSITION INCLUDING ESTERIFIED
COPOLYMER AND DIENE RUBBER COPOLYMER****FIELD OF INVENTION**

[0001] The exemplary embodiment relates to a lubricating composition comprising an esterified copolymer and a diene rubber copolymer. The lubricating composition finds particular application in engine oils, such as crankcase oils. Also disclosed are a method and a use of the lubricating composition.

BACKGROUND

[0002] Viscosity modifiers (also known as viscosity index (VI) improvers) are often added to lubricating oil compositions to improve the viscosity index of the lubricant. The viscosity modifier is combined, in the lubricating oil composition, with a base oil, together with other performance additives, such as dispersants, detergents, friction modifiers, corrosion inhibitors, pour point depressants, and so forth, depending on the particular application. Typical viscosity modifiers include polymers of alkyl methacrylates, alkyl acrylates, olefins (such as copolymers of ethylene and propylene), copolymers of styrene and conjugated dienes, and copolymers of maleic anhydride with alpha-olefins or styrene, and their esterified derivatives. Viscosity modifiers comprising ester groups tend to incorporate ester functional groups in pendent/grafted/branched groups. The ester functional groups may be derived from linear or branched alkyl alcohols with 1 to 40 carbon atoms. Examples of such 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 International Application Nos. WO 07/133999 and WO 2010/014655.

[0003] Lubricating oils are often subjected to high temperatures and high shear conditions in portions of a vehicle engine, such as the bearings.

Under certain conditions, a viscosity modifier can be mechanically degraded by the moving parts and partially lose its ability to increase the viscosity of the base oil. The degradation causes lowered lubricant film thickness, which can, in turn, lead to accelerated wear. The shear stability of viscosity modifiers tends to increase as the molecular weight decreases. However, the thickening capability of the viscosity modifier also decreases as the molecular weight decreases.

[0004] Compositions have been formulated to achieve minimum high temperature/high shear rate (HTHS) viscosity while protecting against excessive wear in internal combustion engines. High HTHS viscosity lubricating compositions, although good for wear protection, tend to suffer from poor fuel economy. By contrast, fluids with relatively low HTHS viscosities typically also exhibit low kinematic viscosity (KV), resulting in formation of a thinner lubricating film, which can improve fuel economy but negatively impact wear protection.

[0005] So for either enhanced wear protection, or for improved fuel efficiency, it is advantageous for the ratio of HTHS/KV to be as high as possible. With this relationship it would be possible to formulate, 1) lubricating oils with the same KV but higher HTHS, or in other words, to have the same fuel efficiency but improved wear protection, 2) lubricating oils with the same HTHS but reduced KV, i.e. the same wear protection but improved fuel efficiency, and 3) reduce KV but increase HTHS.

[0006] For SAE 30 grade engine oils, the lubricating composition can have a kinematic viscosity (KV₁₀₀) of from 9.3 to 12.5 cSt as defined in SAE J300, "Engine Oil Viscosity Classification." Such lubricating compositions can have a KV₄₀ from about 50 to about 70 cSt and must have an HTHS viscosity greater than 2.9 cSt.

[0007] Some engine oils are preferably formulated with the use of a diene rubber copolymer to meet the foregoing engine performance requirements, and these formulations generally have no problem meeting

the HTHS viscosity limits, for example, of 2.9 cP minimum for the SAE 10W-30 grade. However, to maximize bearing durability, it is often desired to formulate SAE 30 grade engine oils with HTHS viscosity of at least 3.4 cP or at least 3.45 cP or at least 3.5 cP. For example, a number of European original equipment manufacturers (OEM) require a higher minimum HTHS requirement of 3.5 cP for the 10W-30 viscosity grade and formulating an engine oil with a diene rubber copolymer to achieve such specifications can be challenging.

[0008] It would be desirable to provide a lubricating composition that includes a diene rubber and to give a combination that provides good HTHS for durability of engine components while providing a low kinematic viscosity to reduce friction and improve fuel economy.

BRIEF DESCRIPTION OF THE FIGURES

[0009] Figure 1 shows is a graphical view of the ratio of HTHS:kinematic viscosity from the data in tables 2 and 3 in Example 2

BRIEF DESCRIPTION

[0010] In one aspect of the exemplary embodiment, a lubricating composition includes (A) an esterified copolymer comprising units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer, the vinyl monomer comprising a vinyl aliphatic monomer, the carboxylic acid monomer comprising an ethylenically unsaturated carboxylic acid or derivative thereof, esterified with a primary alcohol (linear or branched); and (B) a diene rubber copolymer comprising at least a first block (B1) derived from a conjugated diene monomer and at least a second block (B2) derived from a vinyl aromatic monomer. A ratio of the diene rubber copolymer to the esterified copolymer in the lubricating composition (B:A) is from 0.01 to 0.9, by weight.

[0011] In another aspect, a process for preparing a lubricating composition includes admixing (A) an esterified copolymer with (B) a diene rubber

copolymer, (C) an oil of lubricating viscosity and (D) optionally one or more other performance additives. The esterified copolymer includes units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer. The vinyl monomer includes a vinyl aliphatic monomer. The carboxylic acid monomer includes an ethylenically unsaturated carboxylic acid or derivative thereof, esterified with a primary alcohol (linear or branched). The diene rubber copolymer includes at least a first block (B1) derived from a conjugated diene monomer and at least a second block (B2) derived from a vinyl aromatic monomer. A ratio, by weight, of the diene rubber copolymer to the esterified copolymer in the lubricating composition (B:A) is from 0.01 to 0.9.

DETAILED DESCRIPTION

[0012] A method for determining viscosity index (VI) of a lubricating composition is according to the procedure outlined in ASTM D2270, "Standard Practice for Calculating Viscosity Index From Kinematic Viscosity at 40 and 100°C," ASTM International, West Conshohocken, PA, DOI: 10.1520/D2270-10E01.

[0013] The kinematic viscosity (KV) is according to ASTM D445. The KV can be expressed as KV₁₀₀ or KV₄₀ (KV refers to Kinematic Viscosity, and 100 or 40 refers to the Celsius temperature at which the viscosity of the oil is measured). Unless otherwise noted, KV values are determined by this method and are reported in Centistokes (cSt). 1 cSt = 1 mm²/s.

[0014] A method for determining the High Temperature High Shear (HTHS) viscosity of a lubricating composition is according to the procedure ASTM D4683-10, "Standard Test Method for Measuring Viscosity of New and Used Engine Oils at High Shear Rate and High Temperature by Tapered Bearing Simulator Viscometer at 150°C," ASTM International, West Conshohocken, PA. This test method determines the viscosity of an oil at 150°C and $1.0 \cdot 10^6 \text{ s}^{-1}$ using a viscometer having a slightly tapered rotor and stator called the Tapered Bearing Simulator (TBS) Viscometer.

Unless otherwise noted, HTHS values are determined by this method and are reported in centipoise (cP). 1 centipoise = 1 mPa-second.

[0015] For some applications, the lubricating composition can have a ratio of kinematic viscosity (KV₁₀₀) to HTHS of up to 2.6-3.6.

[0016] The viscosity at low temperatures can be measured using the Cold Crank Simulator (CCS) test, as described in ASTM method D5293 – 10, “Standard Test Method for Apparent Viscosity of Engine Oils Between -5 and -35°C Using the Cold-Cranking Simulator,” DOI: 10.1520/D5293-10 ASTM International, West Conshohocken, PA. For SAE 0W oils, the lubricating composition must have a CCS viscosity at -35°C, determined according to this method, of less than 6200 cP according to SAE J300.

[0017] The inventors have found that the combination of an esterified copolymer with a diene rubber can provide a synergistic effect with respect to providing a lubricant with at least one (or at least two, or all) of acceptable or improved HTHS, KV, shear stability, acceptable or improved viscosity index control, and acceptable or improved low temperature viscosity.

[0018] Accordingly, an exemplary engine oil lubricating composition includes (A) an esterified copolymer, (B) a diene rubber copolymer, and (C) an oil of lubricating viscosity. The esterified copolymer (A) is formulated to provide the lubricating composition with a high ratio of high temperature/high shear rate (HTHS) to kinematic viscosity (KV). The diene rubber copolymer includes units derived from a conjugated diene monomer and units derived from a vinyl aromatic monomer. The resulting lubricating composition can have improved wear protection while providing low kinematic viscosity for improved fuel efficiency.

[0019] The exemplary lubricating composition finds use as an engine oil in an internal combustion engine, such as a motor vehicle engine. In one embodiment, the lubricating composition is used as a crankcase lubricant. A crankcase lubricant is an oil used for general lubrication in an internal

combustion engine where an oil sump is situated generally below the crankshaft of the engine and to which circulated oil returns.

[0020] A ratio (B:A) of the diene rubber copolymer (B) to the exemplary viscosity modifier (esterified copolymer) (A) in the lubricating composition can be for example, from 0.01 to 0.9 or 0.2-0.85, or 0.3-0.8, or at least 0.4, expressed by weight.

[0021] An exemplary lubricating composition can include from 0.1 to 50 wt. %, or 1.0 to 20 wt. %, or 1.5 to 10 wt. % of the exemplary viscosity modifier (A), such as less than 5 wt. % of the viscosity modifier.

[0022] The exemplary lubricating composition can include from 0.1 to 10 wt. %, or 0.2 to 5 wt. % of the diene rubber copolymer (B), such as from 0.5 to 1.5 wt. %.

[0023] In another aspect, a lubricating composition in accordance with the exemplary embodiment can be formed by admixing (A) a viscosity modifier with (B) a diene rubber copolymer, (C) an oil of lubricating viscosity (which may be referred to herein as a base oil), and (D) optionally one or more other performance additives.

[0024] In another aspect, a lubricant concentrate in accordance with the exemplary embodiment can be formed by admixing (A) a viscosity modifier with (B) a diene rubber copolymer, (C) optionally, an oil of lubricating viscosity, in a lesser amount than in the lubricating composition, and (D) optionally one or more other performance additives.

[0025] In another aspect of the exemplary embodiment, a use of the lubricating composition described herein in an internal combustion engine includes providing the engine with the lubricating composition.

[0026] In another aspect of the exemplary embodiment, a method of providing a lubricating composition with at least one (or at least two, or up to all) of acceptable or improved shear stability, acceptable or improved viscosity index control, acceptable or improved oxidation control, and acceptable or improved low temperature viscosity includes providing the

lubricating composition with an esterified copolymer (A) and a diene rubber copolymer (B) at a ratio of the diene rubber copolymer to the exemplary viscosity modifier component (B:A) in the lubricating composition of, for example, from 0.01 to 0.9 or 0.2 to 0.85, or 0.3-0.8, or at least 0.4, by weight. This provides a lubricating composition with at least one (or at least two, or all) of acceptable or improved shear stability, acceptable or improved viscosity index control, acceptable or improved low temperature viscosity and acceptable or improved oxidation control.

I. The Viscosity Modifier (A)

[0027] The exemplary viscosity modifier is an esterified copolymer. The exemplary esterified copolymer (A) disclosed herein includes a polymeric backbone comprising units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer, which can be an ethylenically unsaturated carboxylic acid or derivative thereof. The vinyl monomer can be selected from polymerizable aromatic and aliphatic vinyl monomers. Exemplary aliphatic vinyl monomers include alpha-olefins. By way of example, the exemplary copolymer can include a polymeric backbone derived from 1-dodecene and maleic anhydride, as the carboxylic acid monomer.

[0028] 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 monomer and the carboxylic acid monomer. Pendent groups may be grafted to the backbone. The carboxylic acid monomer units on the backbone may be esterified and/or amidized/imidized.

[0029] In general, the polymeric backbone can be an alternating structure whereby each carboxylic acid unit is spaced from the next carboxylic acid unit by at least one unit derived from a vinyl monomer, such as an alpha-olefin. The exemplary esterified copolymer can have at least 20 or at least 100 units derived from these monomers in its backbone. In one embodiment, the backbone chain of monomer units derived from the selected

monomers is of no more than 10,000 such monomer units, or no more than 1000 such monomer units.

[0030] A molar ratio of the vinyl monomer units (A1) to carboxylic acid monomer units (A2) in the copolymer can be for example, from 1:3 to 3:1 or from 1:2 to 2:1, or 0.6:1 to 1:1. 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.

[0031] The copolymer backbone optionally includes units derived from monomers other than the vinyl monomer (A1) and carboxylic acid monomer (A2) disclosed herein. For example, the backbone may include units derived from one or more monomers capable of polymerizing with one or both of the vinyl monomer and carboxylic acid monomer such as acrylates or methacrylates. In one embodiment, units derived from these other monomers constitute no more than 30 mole % or no more than 20 mole % or no more than 10 mole % of the monomer derived units in the copolymer. For example, 1-5% of the units in the backbone may be formed from these other monomers.

[0032] The exemplary esterified copolymer further includes ester pendent groups formed, for example, by esterification of carboxylic acid units of the copolymer with a primary alcohol, such as one or more of a linear alcohol and a branched alcohol, cyclic or acyclic alcohol, or a combination thereof.

[0033] The exemplary esterified copolymer may further include a nitrogen containing group (such as amino-, amido- and/or imido- group, or a nitrogen containing salt).

[0034] In one embodiment, the ester groups and nitrogen containing groups (such as amino-, amido- and/or imido- group) are 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. %) nitrogen to the esterified copolymer.

[0035] 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, or 5000 to 30,000, or 5000 to 25,000, or 10,000 to 17,000. The M_w of the exemplary polymer, before esterification, can also range from about 5000 to 10,000, or 12,000 to 18,000, or 9000 to 15,000, or 15,000 to 20,000, or 8000 to 21,000, and in one embodiment, may be at least 10,000. The M_w of the exemplary esterified 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 35,000.

A. The Vinyl Monomer Units of the Viscosity Modifier

[0036] The esterified copolymer (A) includes vinyl monomer units (A1) derived from at least one of a vinyl aromatic monomer or a vinyl aliphatic monomer. In one embodiment, the vinyl monomer units at least include units derived from the vinyl aliphatic monomer.

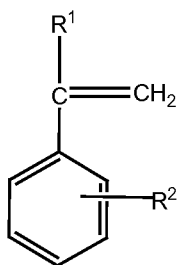
[0037] Where both are present, the arrangement of vinyl monomer units in the backbone can be largely random and depend on the ratio of the two vinyl monomers.

[0038] 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 C_6 - C_{30} alpha-olefins such C_8 - C_{20} alpha-olefins, or C_{10} - C_{18} alpha-olefins, or C_{10} - C_{14} 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. In an embodiment, the vinyl aliphatic

monomer is a hydrocarbon and does not contain a heteroatom, such as O, N or S. In an embodiment, the vinyl aliphatic monomer is an alpha-olefin.

[0039] An exemplary vinyl aromatic monomer, where present, is a polymerizable aromatic monomer, specifically, an aromatic compound substituted with a vinyl group ($-\text{CH}=\text{CH}_2$).

[0040] 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, vinylnaphthalene, and mixtures of these. Specific examples include styrene, alpha-methylstyrene, alpha-ethylstyrene, alpha-isopropylstyrene, *p*-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-alpha-methylstyrene, *p*-isopropyl-alpha-methylstyrene, *m*-isopropylstyrene, *p*-isopropylstyrene, vinylnaphthalene, and mixtures thereof.

[0041] In the exemplary embodiment, a majority of the vinyl monomer units of A1 (at least 50% of the vinyl monomer units or at least 80%, or at least 90%, or 100% of the vinyl monomer units) are derived from the vinyl aliphatic monomer.

B. The Carboxylic Acid Units of the Viscosity Modifier

[0042] The exemplary ethylenically unsaturated carboxylic acid or derivative thereof used in forming the carboxylic acid units (A2) of the exemplary esterified copolymer (A) may be a mono- or 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.

[0043] Exemplary unsaturated α,β - ethylenically 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.

[0044] 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.

[0045] Other suitable monomers for forming the carboxylic acid monomer unit of the exemplary esterified copolymer are described in U.S. Pub. No. 20090305923.

C. Alcohols for Esterification of the Carboxylic Acid Unit

[0046] The carboxylic acid unit of the exemplary esterified copolymer (A) 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.

[0047] Suitable primary alcohols for use herein may contain 1 to 150 carbon atoms, or 4 to 50, 2 to 20, or 8 to 20 (such as 4 to 20, or 4 to 16, or 8 to 12) carbon atoms. The primary alcohol may be linear or may be branched at the α -, or β -, or higher position, cyclic or acyclic, or a combination thereof. 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 the β - or higher position.

[0048] In one embodiment, 10, 20, or 30 to 100 mole %, alternatively 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 alkyl group (that is, in the alcohol-derived or alkoxy portion of the ester) and 70 or 80 to 0 mole %, alternatively 80 to 30 mole %, based on the total number of moles of carboxyl groups in the esterified copolymer, contain ester groups having 8 to 10 carbon atoms in the alcohol portion. In one embodiment, the ester 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.

[0049] In one embodiment, 0.1 to 99.89 (or 1 to 90, or 2 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 90, or 2 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, 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.

[0050] Examples of useful primary alcohols include butanol, heptanol, octanol, 2-ethylhexanol, decanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, and combinations thereof.

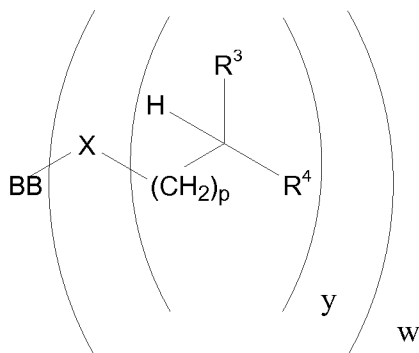
[0051] Other exemplary primary alcohols include commercially available mixtures of alcohols. These include oxoalcohols which may comprise, for example, various mixtures of alcohols having from 8-24 carbon atoms. Of the various commercial alcohols useful herein, one contains 8 to 10 carbon atoms, and 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.

[0052] 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.

[0053] 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).

[0054] In one embodiment, 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 derived from the carboxylic acid monomer units and vinyl monomer units, i.e. the carbon backbone not including the carboxyl group;

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 –CH₂–), 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);

R³ and R⁴ are independently linear or branched hydrocarbyl groups, and the combined total number of carbon atoms present in R³ and R⁴ is at least 12 (or at least 16, or at least 18 or at least 20).

[0055] In different embodiments the copolymer with pendent groups may contain 0.10% to 100%, or 0.5% to 20%, or 0.75% to 10%, 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”.

[0056] In different embodiments the functional groups defined by X in Formula II above, may comprise at least one of -CO₂-, -C(O)N= or -(CH₂)_v-, wherein v is an integer in the range of 1 to 20, or 1 to 10, or 1 to 2.

[0057] In one embodiment X is derived from an α,β -ethylenically unsaturated dicarboxylic acid or derivatives thereof. Examples of suitable carboxylic acids or derivatives thereof may include maleic anhydride, maleic acid, (meth)acrylic acid, itaconic anhydride, or itaconic acid. In one embodiment, the ethylenically unsaturated carboxylic acid or derivatives thereof may be at least one of maleic anhydride and maleic acid.

[0058] In one embodiment X is other than an alkylene group, connecting the copolymer backbone and the branched hydrocarbyl groups.

[0059] In different embodiments the pendent groups may be esterified, amidated or imidated functional groups.

[0060] 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- C_{1-15} alkyl-decyl groups (e.g., 2-octyldecyl) and 2,4-di- C_{1-15} alkyl-decyl groups (e.g., 2-ethyl-4-butyl-decyl); alkyl groups containing C_{1-5} 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 C_{5-17} α -olefin oligomers (from dimer to hexamer).

[0061] The pendent groups in Formula II may contain a total combined number of carbon atoms on R^3 and R^4 in the range of 12 to 60, or 14 to 50, or 16 to 40, or 18 to 40, or 20 to 36.

[0062] Each of R^3 and R^4 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 R^3 and R^4 group may be 10 to 24.

[0063] 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.

[0064] 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.

D. Nitrogen-Containing Group of the Viscosity Modifier

[0065] The exemplary esterified copolymer (A) 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 with a nitrogen containing reactant, such as an amine, to form a salt, amide, imide, or mixture thereof.

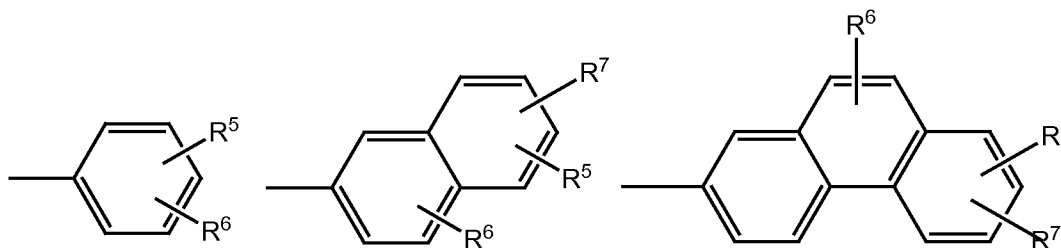
[0066] Examples of suitable nitrogen-containing compounds capable of being incorporated into the copolymer include N,N-dimethylacrylamide, N-vinyl carbonamides, such as, N-vinyl-formamide, N-vinylacetamide, N-vinyl propionamides, N-vinyl hydroxyacetamide, vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminobutyl acrylamide, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, dimethylaminoethyl acrylamide, and mixtures thereof.

[0067] 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 or amine groups.

[0068] 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.

[0069] 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, pentaethylenehexamine, diethylenetriamine, triethylenetetramine, and polyethyleneimine.

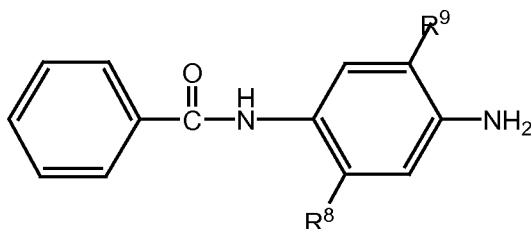
[0070] In another embodiment, the nitrogen containing group may be derived from an amine which is aromatic. Aromatic amines include those which can be represented by the general structure $\text{NH}_2\text{-Ar}$ or T-NH-Ar , where T may be alkyl or aromatic, Ar is an aromatic group, including nitrogen-containing 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, -H, -C₁₋₁₈ alkyl groups, nitro groups, -NH-Ar, -N=N-Ar, -NH-CO-Ar, -OOC-Ar, -OOC-C₁₋₁₈ alkyl, -COO-C₁₋₁₈ alkyl, -OH, -O-(CH₂CH₂-O)_nC₁₋₁₈ alkyl groups, and -O-(CH₂CH₂O)_nAr (where n is 0 to 10).

[0071] 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-butaniline, 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.

[0072] 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, aminopyrimidines, mercaptotriazoles, aminophenothiazines, aminopyridines, aminopyrazines, aminopyrimidines, pyridines, pyrazines, pyrimidines, aminothiadiazoles, aminothiathiadiazoles, 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 R⁸ and R⁹ are independently alkyl or alkoxy groups such as methyl, methoxy, or ethoxy.

[0073] In one instance, R⁸ and R⁹ are both –OCH₃ and the material is known as Fast Blue RR [CAS# 6268-05-9]. In another instance, R⁹ is –OCH₃ and R⁸ is –CH₃, and the material is known as Fast Violet B [99-21-8]. When both R⁸ and R⁹ 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. 20030030033, 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 sp² hybridized within an aromatic ring.

[0074] 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 (ADPA), 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.

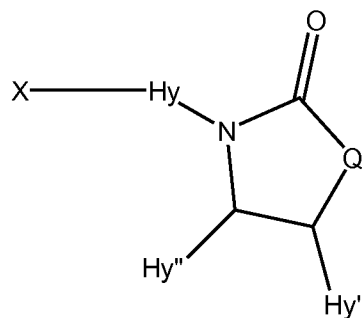
[0075] In one embodiment, the amine component of the copolymer further includes an amine having at least two N-H groups capable of condensing with the carboxylic functionality of the copolymer. This material is referred to hereinafter as a "linking amine" as it can be employed to link together two of 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 aromatic amines having three or more aromatic rings, such as formaldehyde coupled ADPA or similar type aromatic amines disclosed in WO2011146692 to the Lubrizol Corporation, published

November 24, 2011, for example, at paragraphs [0068 to [0080]. Other examples of linking amines can include ethylenediamine, phenylenediamine, and 2,4-diaminotoluene; others include propylenediamine, hexamethylenediamine, and other, α - 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.

[0076] In one embodiment, the amine includes nitrogen-containing compounds capable of reacting directly with a copolymer backbone. Examples of suitable amines include *N*-*p*-diphenylamine, 4-anilinophenyl methacrylamide, 4-anilinophenyl maleimide, 4-anilinophenyl itaconamide, acrylate and methacrylate esters of 4-hydroxydiphenylamine, and the reaction product of *p*-aminodiphenylamine or *p*-alkylaminodiphenylamine with glycidyl methacrylate.

[0077] 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.

[0078] 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;

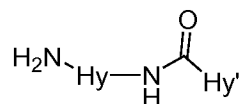
Hy'' is hydrogen, or a hydrocarbyl group (typically alkyl, or C₁₋₄-, or C₂-alkyl);

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.

[0079] 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.

[0080] In one embodiment, the amide may be represented by the general structure:



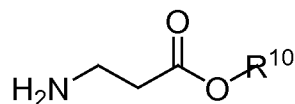
wherein:

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).

[0081] Examples of a suitable amide include N-(2-amino-ethyl)-acetamide, or N-(2-amino-propyl)-acetamide.

[0082] In one embodiment, the β -alanine alkyl esters may be represented by the general structure:



wherein:

R^{10} is an alkyl group having 1 to 30, or 6 to 20 carbon atoms.

[0083] 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.

[0084] 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.

[0085] In one embodiment, the copolymer may be reacted with an amine-containing compound selected from morpholines, imidazolidinones, and mixtures thereof. 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.

[0086] 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. %) nitrogen to the copolymer.

E. Formation of the Esterified Copolymer (A)

[0087] The esterified copolymer (A) can be formed by a method which includes:

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

(2) optionally, esterifying the copolymer backbone 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 whereby the resulting copolymer (A) is esterified in at least one of (1), (2), and (3).

1. Formation of the Copolymer Backbone

[0088] The copolymer backbone of the esterified copolymer (A) 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 and other properties of the exemplary copolymer.

[0089] The copolymer backbone may be prepared by reacting the carboxylic acid monomer with the vinyl monomer.

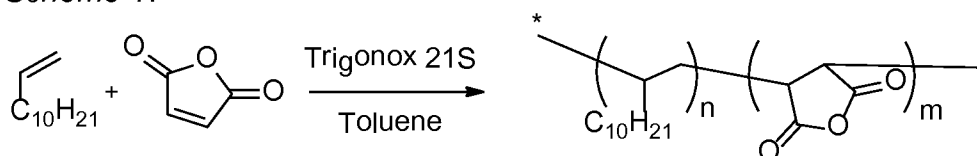
[0090] The solvent can be a liquid organic diluent. Generally, the solvent has as a boiling point that is high enough to provide the required reaction temperature. Illustrative diluents include toluene, t-butyl benzene, benzene, xylene, chlorobenzene, various petroleum fractions boiling above 125°C, and mixtures thereof.

[0091] 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.

[0092] 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.

[0093] Copolymerization of 1-dodecene and maleic anhydride in toluene under conventional free radical polymerization techniques leads to a low molecular weight copolymer.

2. Esterification of the Copolymer Backbone

[0094] Esterification (or transesterification, when the copolymer backbone already contains ester groups and those of a different type are desired) of the exemplary copolymer backbone 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.

[0095] In one embodiment, at least 2%, or at least 5%, or in certain embodiments 10% to 20%, of the carboxy functions of the copolymer remain un-converted to ester groups. Most of these 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 90 to 99% 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.

3. Formation of Nitrogen-containing Groups on the Copolymer backbone

[0096] 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 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.

[0097] 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.

[0098] 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 derived group 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.

[0099] In another embodiment, the nitrogen-containing compound may be a monomer that can polymerize with both the vinyl 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. The Diene rubber copolymer (B)

[0100] The exemplary diene rubber copolymer (B) in the exemplary lubricating composition includes a polydiene component (B1), derived from a diene monomer, and a polyvinyl aromatic component (B2), (a poly(vinyl arene)), derived from a vinyl aromatic monomer. The exemplary diene rubber copolymer comprises a block copolymer including one or more blocks, at least one of which is predominantly polydiene (B1) (e.g., at least 50% of the units are derived from a diene monomer or monomers), and one or more poly(vinyl aromatic) blocks, at least one of which is predominantly poly(vinyl arene) (B2) (e.g., less than 50% of the units are derived from a vinyl aromatic monomer or monomers).

[0101] The M_w of the diene rubber copolymer (B) can be 30,000 to less than 200,000, or 100,000 to 200,000, or 30,000 to 100,000. In one embodiment, the diene rubber copolymer M_w is at least 30,000, or at least 50,000, or at least 80,000 or at least 100,000. In one embodiment, the diene rubber copolymer M_w is 100,000 to 150,000, e.g., about 120,000.

[0102] The polydispersity (M_w / M_n ratio) of certain suitable block polymers (B) is typically between 1.0 and 1.2.

[0103] The vinyl aromatic monomer content of the diene rubber copolymer (B) is typically 10% to 60% by weight, or 15 to 60%, or 30 to 60% by weight. The diene monomer content (remaining content) of these copolymers is typically 40% to 90%, or 40 or 50% to 85 or 70% by weight.

A. The Diene Monomer of the Diene rubber copolymer

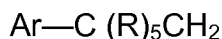
[0104] Dienes contain two double bonds, commonly located in conjugation in a 1,3 relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered to be included within the definition of "dienes" as used herein.

[0105] Suitable diene monomers for forming the polydiene component (B1) of the diene rubber copolymer (B) include conjugated dienes containing from 4 to 20 carbon atoms. Exemplary diene monomers include 1,3-conjugated dienes, such as butadiene, 2-methyl-1,3-butadiene (isoprene), piperylene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, chloroprene, and mixtures thereof. In one embodiment, the diene monomer includes 4-6 carbon atoms, such as 1,3-butadiene. For example, the diene rubber copolymer includes one or more polydiene blocks derived from 1,3-butadiene, randomly copolymerized butadiene and isoprene, or one or more blocks of each of butadiene and isoprene, although it is generally the case that the polydiene block(s) in the diene rubber copolymer are homopolymer blocks. Star copolymers are also contemplated.

[0106] In one embodiment, the polydiene component (B1) has a M_w of at least about 10,000, or at least 20,000. The polydiene component (B1) can have a M_w of up to about 200,000, or up to 150,000, or up to 100,000.

B. The Vinyl Aromatic Monomer of the Diene rubber copolymer

[0107] Suitable vinyl aromatic monomers for forming the poly (vinyl aromatic) component (B2) of the diene polymer (B) are of the general formula:



wherein R is hydrogen or alkyl, Ar is an aromatic ring structure having from 1 to 3 aromatic rings with or without alkyl, halo, or haloalkyl substitution, and wherein any alkyl group contains 1 to 6 carbon atoms, which may be mono- or multi-substituted with functional groups such as halo, nitro, amino, hydroxy, cyano, carbonyl and carboxyl. In one embodiment, Ar is phenyl or alkylphenyl, halophenyl, alkylphenyl, alkylhalophenyl, naphthyl, pyridinyl, or anthracenyl. The vinyl substituted aromatics generally contain from 8 to about 20 carbons, or from 8 to 12 carbon atoms, such as 8 or 9 carbon atoms.

[0108] In one embodiment, Ar is phenyl or alkyl phenyl. Exemplary vinyl aromatic monomers include styrene, alpha-lower alkyl substituted styrenes, for example, alpha-methylstyrene and alpha-ethyl styrene, styrenes having ring substituents, such as lower alkyl ring substituents, for example, o-methyl styrene, m-methyl styrene, p-methyl styrene, and p-tert-butylstyrene, vinyl benzene sulfonic acid, and p-lower alkoxy styrene, 1,3-dimethyl styrene, vinyl toluenes such as p-vinyltoluene, ethyl styrenes, propyl styrenes, butyl styrenes, vinyl biphenyl, vinyl naphthalene, vinyl anthracene, vinyl substituted aromatics including substituted vinyl anthracenes, substituted vinyl naphthalenes and substituted vinyl benzenes (styrenes) including substituted styrenes, and mixtures thereof. Substituted styrenes include styrenes that have substituents on the ring or on the vinyl group. Such substituents include halo-, amino-, alkoxy-, carboxy-, hydroxy-, sulfonyl-, hydrocarbyl- wherein the hydrocarbyl group has from 1 to about 12 carbon atoms, and other substituents. Mixtures of two or more vinyl aromatic monomers can be used. In one embodiment, the vinyl aromatic monomer is selected from styrene, alpha-methylstyrene, nuclear methylstyrenes (such, as 2-, 3-, or 4- methylstyrene), ethylstyrene, isopropylstyrene, tert-butylstyrene, chlorostyrenes, dichlorostyrenes, vinyl naphthalene and mixtures of these. Suitable vinyl aromatic monomers

are those corresponding to Formula I above. In one embodiment, styrene or a substituted styrene is used.

[0109] For example, the vinyl aromatic block(s) may be derived solely from styrene or form from randomly copolymerized styrene and another vinyl aromatic monomer, such as alpha-methyl styrene, although the blocks are generally homopolymer blocks. Where more than one polyvinyl aromatic block is present, the blocks may be derived from the same or different monomer(s).

[0110] The weight average molecular weight (M_w) of each poly(vinyl aromatic) block can be from about 3,000 to about 40,000 and in one embodiment, less than 20,000. The M_w can be measured by gel permeation chromatography (GPC) in THF on a machine calibrated with polystyrene standards. Where there is more than one poly(vinyl aromatic) block, at least one of the poly(vinyl aromatic) blocks has a M_w of at least 5,000.

[0111] Hydrogenated styrene/diene block copolymers, in particular, are useful. In a hydrogenated aromatic/diene block copolymer, it is typically the diene monomer-containing block that is selectively hydrogenated, the aromatic portion being generally more resistant to hydrogenation.

C. Formation of the Diene rubber copolymer (B)

[0112] Methods of polymerizing dienes and vinyl aromatic compounds in the presence of chain transfer agents, initiators, and/or comonomers are well known and any suitable method may be utilized in preparing the diene rubber copolymer used in the exemplary lubricating composition. A polybutadiene/polystyrene copolymer can be prepared, for example, by anionic polymerization of butadiene and styrene in the presence of an initiator, such as an alkyl lithium, e.g., butyl lithium. For example, a charge of a first monomer is polymerized in a reactor in the presence of an anionic initiator in a suitable solvent at a suitable reaction temperature, to form a first block. A charge of a second monomer is introduced to the reactor and allowed to copolymerize with the first block at a suitable reaction

temperature to form a diblock. The first monomer is either a diene monomer or a vinyl aromatic monomer, and the second monomer the other of the diene and vinyl aromatic monomers. It will be appreciated that further charges of monomer may be added to form triblock or multiblock polymers. Block copolymers made by consecutive addition of styrene to give a relatively large homopolymer segment (B2), followed by a diene to give a relatively large homopolymer segment (B1), are exemplary.

[0113] Suitable solvents for the reaction include normally liquid organic materials which form a solution with the monomers, copolymers, and diene rubber copolymer. Exemplary solvents include aromatic and substituted aromatic hydrocarbons such as benzene, ethylbenzene, toluene, and xylene, substituted or unsubstituted, straight or branched chain saturated aliphatics of 5 or more carbon atoms, such as heptane, hexane, and octane, and alicyclic or substituted alicyclic hydrocarbons having 5 or 6 carbon atoms, such as cyclohexane.

[0114] Hydrogenation of the unsaturated block polymers initially obtained produces polymers that are more oxidatively and thermally stable. Reduction is typically carried out as part of the polymerization process, using finely divided, or supported, nickel catalyst. Other transition metals may also be used to effect the transformation. Hydrogenation is normally carried out to reduce approximately 95-99.5% of the olefinic unsaturation of the initial polymer. For reasons of oxidative stability, a hydrogenated copolymer (B) may be formed which has no more than 5%, or no more than 0.5% residual olefinic unsaturation on the basis of the total amount of olefinic double bonds present in the polymer (B) prior to hydrogenation. Such unsaturation can be measured by a number of means, such as infrared or nuclear magnetic resonance spectroscopy.

III. The Engine Oil Lubricating Composition

[0115] An engine oil lubricating composition according to one aspect of the present invention includes the esterified copolymer (A), the diene rubber

copolymer (B), an oil of lubricating viscosity (or “base oil”) (C), and optionally other performance additives, such as other viscosity modifiers, dispersants, detergents, extreme pressure agents, antiwear agents, antiscuffing agents, pour point depressants, corrosion inhibitors, and the like.

[0116] 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. %, or at least 60 wt. % of the lubricating composition.

[0117] In one embodiment, the esterified copolymer (A) is at least 0.1 wt. %, or at least 1 wt. %, or up to 10 wt. % or up to 5 wt. % of the lubricating composition.

[0118] The exemplary lubricating composition can include from 0.1 to 10 wt. %, or 0.2 to 5 wt. % of the diene rubber copolymer (B), such as from 0.5 to 1.5 wt. %.

[0119] The base oil (C) in the lubricating composition can be for example, from 10 to 95 wt. %, or 20-80 wt. %. Other performance additives (other than the viscosity modifier (A) and diene rubber copolymer (B)) can be for example, from 0.2 to 40 wt. %, or 0.5-5 wt. % of the lubricating composition.

[0120] An exemplary lubricating composition includes at least 1 wt. % of the exemplary viscosity modifier (A), at least 0.2 wt. % of the diene rubber copolymer (B), at least 40 wt. % of a polyalphaolefin (PAO)-based base oil (C), optionally, a pour point depressant at less than 1 wt. %, and optionally one or more performance additives.

A. Formation of the Lubricating Composition

[0121] A lubricating composition can be formed by combining the esterified copolymer (A) with the diene rubber copolymer (B), a base oil (C), and optionally other performance additives. In one embodiment, a process for preparing the exemplary lubricating composition comprises:

(1) forming (or obtaining) the esterified copolymer (A), as described above, and

(2) mixing the esterified copolymer formed in (1) with a diene rubber copolymer (B), an oil of lubricating viscosity (C), and optionally one or more performance additives, other than the esterified copolymer (A) and diene rubber copolymer (B), in sufficient amounts to provide a lubricating composition in which the ratio of the diene rubber copolymer (B) to the exemplary viscosity modifier (A) component (B:A) in the lubricating composition or lubricant concentrate is from 0.01 to 0.9 or 0.2 to 0.85, or 0.3 to 0.8, or at least 0.4.

IV. Oil of Lubricating Viscosity

[0122] Suitable oils of lubricating viscosity (C) include natural and synthetic oils, oils derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils, and mixtures thereof.

[0123] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0124] 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.

[0125] 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.

[0126] Natural oils useful in 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.

[0127] 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; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof, and mixtures thereof.

[0128] 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.

[0129] 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.

[0130] In some embodiments, at least 5 wt.%, or at least 10 wt.%, or at least 20 wt.%, or at least 40 wt. % of the lubricating composition is a polyalphaolefin (Group IV).

V. Performance additives

[0131] In one embodiment, the lubricating composition or lubricant concentrate includes at least one performance additive (other than the viscosity modifier and diene rubber copolymer, discussed above, which for convenience of the present description and claims, are not considered “performance additives”). The additional performance additive can include at least one of metal deactivators, detergents, dispersants, extreme pressure agents, antiwear agents, antioxidants, corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, other viscosity modifiers, friction modifiers, seal swelling agents and/or mixtures thereof. In one embodiment, the performance additives may be used alone or in combination.

[0132] The total combined amount of the performance additives present ranges from 0 wt. % to 30 wt. %, or from 1 wt. % to 25 wt. %, or from 2 wt. % to 20 wt. %, or from 3 wt. % to 10 wt. % of the lubricating composition. Although one or more of the performance additives may be present, it is common for the performance additives to be present in different amounts relative to each other.

[0133] In the case of a lubricant concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricating composition), the ratio of the various performance additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 80:20 to 10:90 by weight.

[0134] Exemplary friction modifiers include fatty amines, esters such as borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, fatty imidazolines, condensation products

of carboxylic acids and polyalkylene-polyamines, amine salts of alkylphosphoric acids, molybdenum dithiocarbamate or mixtures thereof.

[0135] Exemplary antioxidants useful as oxidation inhibitors include sulfurized olefins, hindered phenols, diarylamines (such as, diphenylamines e.g., alkylated diphenylamines and phenyl-alpha-naphthylamines), molybdenum dithiocarbamates, and mixtures and derivatives thereof. Antioxidant compounds may be used alone or in combination.

[0136] Exemplary detergents include neutral or overbased, Newtonian or non-Newtonian, basic salts of alkali, alkaline earth and transition metals with one or more of a phenate, a sulfurized phenate, a sulfonate, a carboxylic acid, a phosphorus acid, a mono- and/or a di-thiophosphoric acid, a saligenin, an alkylsalicylate, a salixarate or mixtures thereof.

[0137] 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.

[0138] Exemplary succinimide dispersants can include N-substituted long chain alkenyl succinimides as well as post-treated versions thereof. 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 describe methods for forming such dispersants and their components. Post-treated dispersants include those further treated by reaction with materials such as urea, boron, thiourea, dimercaptiothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides and phosphorus compounds.

[0139] For example such dispersants can be produced by reaction of a C3-C6 polyalkylene (e.g., polypropylene, polyisobutylene, polypentylene,

polyheptylene; most often polyisobutylene) 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.

[0140] Other exemplary dispersants can be derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc.

[0141] Another class of ashless dispersant is acylated polyalkylene polyamines of the type described in U.S. Patent No. 5,330,667.

[0142] 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.

[0143] Antiwear agents can include compounds such as metal thiophosphates, especially zinc dialkyldithiophosphates (ZDDP); phosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides; antiscuffing agents including organic sulfides and polysulfides, such as benzyldisulfide, bis-(chlorobenzyl)disulfide, dibutyl tetrasulfide, di-tertiary butyl polysulfide, di-tert-butylsulfide, sulfurized Diels-Alder adducts, or alkyl sulphenyl N'N'-dialkyl dithiocarbamates.

[0144] 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 dibenzyldisulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, dimercaptothiadiazaoles, 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).

[0145] Exemplary corrosion inhibitors can include octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine; metal deactivators including derivatives of benzotriazoles, thiadiazoles such as dimercaptothiadiazole and its derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, and 2-alkyldithiobenzothiazoles.

[0146] Suitable foam inhibitors include silicones, copolymers of ethyl acrylate and 2-ethylhexylacrylate which optionally further include vinyl acetate; and demulsifiers including polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0147] Pour point depressants, including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides; and seal swell agents including Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil (FN 3200); may also be used in the exemplary lubricating composition or lubricant concentrate.

[0148] In one embodiment, the exemplary lubricating composition or lubricant concentrate is free of sulfurized olefins and amine phosphates. By “free,” it is meant that these ingredients, individually or in combination, amount to less than **0.001%** of the lubricating composition.

[0149] In different embodiments the lubricating composition may include other additives in formulations as described in the following table:

Other Additives	Embodiments (wt %)		
	A	B	C
Dispersant	0.05 to 12	0.75 to 8	0.5 to 6
Antioxidant	0.05 to 1	0.2 to 3	0.5 to 2
Overbased Detergent	0 or 0.05 to 15	0.1 to 10	0.2 to 8
Antiwear Agent	0 or 0.05 to 15	0.1 to 10	0.3 to 5
Friction Modifier	0 or 0.05 to 6	0.05 to 4	0.1 to 2
Viscosity Modifier	0 or 0.05 to 10	0.5 to 8	1 to 6
Any Other Performance Additive	0 or 0.05 to 10	0 or 0.05 to 8	0 or 0.05 to 6

VI. Industrial Application

[0150] The synergistic method employing the esterified copolymer and styrene butadiene rubber (SBR), and the 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, and internal combustion engine oils. It finds particular application as a vehicle engine oil, such as crankcase oil. The exemplary lubricating composition may be supplied to a mechanical device, such as an engine of an automobile, and used for lubrication during normal operation of the mechanical device.

[0151] In several embodiments a suitable engine oil lubricating composition includes the components present (on an active basis) in ranges as shown Table I.

TABLE 1

	Embodiments (wt. % of lubricating composition)		
	A	B	C
Esterified Copolymer	1-25	1-15	1-10
Diene rubber copolymer	0.01-4.0	0.05-2.0	0.1-1.8
Other Performance Additives	0-20	0.5-20	0.5-15
Oil of Lubricating Viscosity	98.89-51.0	98.45-63.0	98.4-73.2
Total of components	100	100	100

[0152] 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 Esterified Copolymer

[0153] A 5L reaction flask was charged with 490.3 g of maleic anhydride (MAA), 841.6 g of 1-dodecene and 860.2 g of toluene. The molar ratio of 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 105 °C.

[0154] A mixture of 6.55 grams of Trigonox®C (a commercially available tert-butyl peroxybenzoate initiator from Akzo Nobel), and 124.5 g of toluene were mixed together and added to the reaction flask over 480 min. via the peristaltic pump. The reaction mixture was stirred at 105 °C for several hours.

[0155] An additional mixture of 19.65 grams of Trigonox®C, and 373.35 g of toluene were mixed together and added to the reaction flask over 480 min. via the peristaltic pump. The reaction mixture was stirred at 105°C for several hours.

[0156] The reaction flask was fitted with a Dean-Stark trap and the reaction mixture heated to 110 °C with stirring. 725 g of Alfol 810™ was added over 80 min and the resulting reaction mixture stirred for 1 hr. An additional 725 g of Alfol 810™ and 34.3 g of a 70% aqueous solution of methane sulfonic acid were added to the reaction flask over 80 min while gradually increasing the reaction temperature to 145°C. After several hours 72g of n-butanol and 17.2 g of 70% aqueous solution of methane sulfonic acid were added and stirred for 3 hr. An additional 72g of n-butanol was added and the reaction stirred for 2 hours. An additional 72g of n-butanol was added and the reaction stirred for several hours. An additional 72g of n-butanol was added and the reaction stirred for 3 to 4 hours. An additional 72g of n-butanol was added and the reaction stirred for 2 to 3 hours. 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 10.15 g of 3-(dimethylamino)-1-propylamine and stirred for an additional 2 hours. 309.1 g of Nexbase 3050 (oil) was added and stirred. The reaction flask was fitted for vacuum stripping and the resultant product vacuum-stripped (-26 in Hg) at 150°C and held for 3 hours. The vacuum was removed and the flask was cooled to 120°C.

[0157] The resulting reaction mixture was filtered twice using fax-5 and filter cloth. GPC run in tetrahydrofuran against polystyrene standards showed a M_w of 24,100, M_n of 16,000.

Example 2: Preparation of Exemplary Lubricating Compositions

[0158] The amine-capped esterified copolymer prepared according to Example 1 was used to prepare lubricating compositions as shown in TABLE 2. All amounts are in wt. %. Samples A and L are comparative examples.

[0159] The esterified copolymer was 98-100 wt.% pure, i.e., the weights shown in Table 2 include minor amounts of reagents from the reaction.

[0160] An 8 weight % solution of a hydrogenated SBR, Lubrizol™ 7408A, in a 5 cSt (100°C) API Group III base oil was used. The SBR solution was obtained by heating the copolymer in base oil to 120°C in the presence of an antioxidant (0.1%, BHT) whilst agitation was provided using a high shear Silverson type mixer.

[0161] A standard commercial engine oil performance package was used as the performance package in all samples.

[0162] A pour point depressant was used in all the examples.

[0163] As the oil of lubricating viscosity, a polyalphaolefin having a kinematic viscosity at 100°C of 4cSt was used (Nexbase 2004).

[0164] B:A is the ratio of the diene rubber copolymer (expressed as undiluted SBR) to the esterified copolymer (expressed as undiluted esterified copolymer) in the lubricating composition, by weight.

TABLE 2

Sample	Esterified Copolymer	8% SBR Soln.	Performance Package	4CSt PAO	Pour Pt. Depressant	B:A Weight Ratio
A	17.33	0	18	64.47	0.2	--
B	16.26	2.45	18	63.09	0.2	0.012
C	13.8	5.1	18	62.9	0.2	0.030
D	11.16	8.0	18	62.64	0.2	0.057
E	10.3	9.4	18	62.1	0.2	0.073
F	8.25	11.12	18	62.43	0.2	0.11
G	4.7	15.8	18	61.3	0.2	0.27
H	3.22	16.29	18	62.29	0.2	0.40
I	2.0	18.5	18	61.3	0.2	0.74
J	1.8	17.8	18	62.2	0.2	0.79
K	1.66	18.8	18	61.34	0.2	0.91
L	0	19.5	18	62.3	0.2	--

[0165] The samples shown in TABLE 2 were tested for various viscometric properties:

[0166] Kinematic viscosity is determined according to ASTM method D445 at 100°C (KV₁₀₀) and at 40°C (KV₄₀), and is expressed in centistokes.

[0167] The viscosity index (VI) at 100°C was measured according to ASTM method D2270.

[0168] High temperature high shear rate viscosity at 150°C was measured according to ASTM method D4683

[0169] Cold Cranking Simulator (CCS) viscosity was obtained at -35°C according to ASTM method D5293 expressed in cP.

TABLE 3

Sample	VISCOSITY @40°C (cSt)	VISCOSITY @100°C (cSt)	VI	HTHS (cP)	CCS @ -35°C (cP)
A	59.16	10.5	169	3.44	8800
B	60.44	10.83	172	3.58	8480
C	59.78	10.77	173	3.48	7820
D	60.06	10.93	176	3.48	7200
E	61.73	11.14	175	3.43	7440
F	60.97	11.17	179	3.52	6660
G	66.03	12.04	182	3.43	6460
H	64.4	11.86	183	3.49	5900
I	68.11	12.49	185	3.42	5890
J	66.51	12.22	184	3.46	5800
K	69.48	12.67	184	3.46	5900
L	68.67	12.61	186	3.51	5550

[0170] Figure 1 shows the effect of the B:A Ratio on the ratio of HTHS viscosity to kinematic viscosity, data from Tables 2 and 3. Namely, Figure 1 shows that the addition of the esterified copolymer to SBR causes a decrease in HTHS/KV100 greater than what would be expected by simple mixing rules. This means that for two oils blended at equal HTHS, adding the esterified copolymer will lead to an increase in KV100 relative to the SBR blended oil alone.

Example 3: Exemplary Lubricating Composition Performance

[0171] A comparison of the effects of the esterified copolymer versus the SBR fluid at equal HTHS is provided below in Table 4.

TABLE 4

		Esterified copolymer of Example 1	Esterified Copolymer of Example 1 plus SBR	SBR
	Group III oil	67.65	69.85	75.42
	Group IV oil		10	
	dispersant		5.6	
	detergent		1.09	
	antiwear agent		0.89	
	antioxidant		1.81	
	anti-foam		0.01	
	friction modifier		0.05	
	demulsifier		0.12	
	Dil Oil		balance	
	Ester of Example 1	8.145	5.805	0
	SBR	0	0.4	1.284
		Kinematic Viscosity		
D2270	VISCOSITY @40 cSt	60.11	62.26	68.04
	VISCOSITY @100 cSt	10.6	10.99	12.13
	VI	168	170	178
		MRV @ -35°C		
D4684 (-35)	MRV @ -35 C cP	17600	17000	15300
	YIELD STRS -35	<35	<35	<35
		Cold Crank Simulator at -30°C		
D5293 (-30)	CCS @ -30 DEGC cP	6470	6060	4950
		High Temperature High Shear		
L-36-90	HTHSR cP	3.49	3.49	3.51

[0172] 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. 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.

[0173] As used herein, the term "(meth) acrylic" and related terms includes both acrylic and methacrylic groups.

[0174] 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.).

[0175] 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.

[0176] 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.

3934-01

What is claimed is:

1. A lubricating composition comprising:

A. an esterified copolymer comprising units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer, the vinyl monomer comprising a vinyl aliphatic monomer, the carboxylic acid monomer comprising an ethylenically unsaturated carboxylic acid or derivative thereof, esterified with a primary alcohol; and

B. a diene rubber copolymer comprising at least a first block (B1) derived from a conjugated diene monomer and at least a second block (B2) derived from a vinyl aromatic monomer; and

wherein a ratio of the diene rubber copolymer to the esterified copolymer in the lubricating composition (B:A) is from 0.01 to 0.9, by weight.

2. The lubricating composition of claim 1, wherein the ratio (B:A) of the diene rubber copolymer to the esterified copolymer in the lubricating composition is from 0.2 to 0.85.

3. The lubricating composition of claim 2, wherein the ratio (B:A) of the diene rubber copolymer to the esterified copolymer in the lubricating composition is from 0.3 to 0.8.

4. The lubricating composition of claim 1, wherein the ratio (B:A) of the diene rubber copolymer to the esterified copolymer in the lubricating composition is at least 0.4.

5. The lubricating composition of claim 1, wherein the esterified copolymer is from 1 to 22 wt. % of the composition, or from 2 to 15 wt. %, or 3-10 wt. %.

6. The composition of claim 1, wherein the diene rubber copolymer is from 0.01 to 18 wt. % of the composition.

7. The lubricating composition of claim 1, wherein the diene monomer from which the at least a first block (B1) of the diene rubber copolymer is derived comprises at least one of butadiene or isoprene.

8. The lubricating composition of claim 1, wherein the vinyl aromatic monomer from which the at least a second block (B2) of the diene rubber copolymer is derived comprises at least one of styrene, alpha-methylstyrene, nuclear methylstyrenes, ethylstyrene, isopropylstyrene, tert-butylstyrene, chlorostyrenes, dichlorostyrenes, or vinylnaphthalene.

9. The lubricating composition of claim 1, wherein the diene rubber copolymer (B) has a weight average molecular weight of at least 30,000.

10. The lubricating composition of claim 1, wherein the at least first block (B1) derived from the conjugated diene monomer has a weight average molecular weight of at least 10,000.

11. The lubricating composition of claim 1, wherein the at least second block (B2) derived from the vinyl aromatic monomer has a weight average molecular weight of at least 3,000.

12. The lubricating composition of claim 1, wherein the diene rubber copolymer (B) comprises at least one of poly(styrene-co-butadiene), poly(styrene-co-butadiene-co-isoprene), or poly(styrene-co-isoprene).

13. The lubricating composition of claim 1, wherein the esterified copolymer (A) has a weight average molecular weight of at least 5000, or up to 50,000.

14. The lubricating composition of claim 1, wherein the units (A1) derived from a vinyl monomer further comprise units derived from a vinyl aromatic monomer.

15. The lubricating composition of claim 1, wherein the vinyl aliphatic monomer comprises an alpha-olefin.

16. The lubricating composition of claim 15, wherein the alpha-olefin has at least 6 carbon atoms.

17. The lubricating composition of claim 1, wherein a molar ratio of the vinyl monomer units to the carboxylic acid monomer units in the copolymer is from 1:3 to 3:1, or from 1:2 to 2:1 or 0.6:1 to 1:1, or from 0.7:1 to 1:1.1.

18. The composition of claim 1, wherein the esterified copolymer is esterified with a primary alcohol branched at the β - or higher position.

19. The composition of claim 1, wherein the carboxylic acid monomer comprises maleic anhydride.

20. The lubricating composition of claim 1, wherein the esterified copolymer (A) comprises a nitrogen-containing group.

21. The lubricating composition of claim 1, wherein at least some of the units (A2) derived from the carboxylic acid monomer are at least one of aminated, amidated, and imidated with a nitrogen-containing compound.

22. The lubricating composition of claim 20, 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.

23. The lubricating composition of claim 1, wherein the lubricating oil comprises a polyalphaolefin API Group IV oil having a kinematic viscosity at 100°C of at least 3 cSt.

24. The lubricating composition of claim 1, wherein the lubricating composition has a kinematic viscosity at 100°C of at least 9.3 cSt or up to 12.5 cSt.

25. The lubricating composition of claim 1, wherein the lubricating composition has a kinematic viscosity at 100°C of at least 6.1 cSt or up to 9.3 cSt.

26. The use of the lubricating composition of any proceeding claims 1 to 24 as an engine oil.

27. A process for preparing a lubricating composition comprising:
admixing (A) an esterified copolymer with (B) a diene rubber copolymer, (C) an oil of lubricating viscosity and (D) optionally one or more other performance additives;

the esterified copolymer comprising units (A1) derived from a vinyl monomer and units (A2) derived from a carboxylic acid monomer, the vinyl monomer comprising a vinyl aliphatic monomer, the carboxylic acid monomer comprising an ethylenically unsaturated carboxylic acid or derivative thereof, esterified with a primary alcohol;

the diene rubber copolymer comprising at least a first block (B1) derived from a conjugated diene monomer and at least a second block (B2) derived from a vinyl aromatic monomer; and

a ratio, by weight, of the diene rubber copolymer to the esterified copolymer in the lubricating composition (B:A) being from 0.01 to 0.9.

28. The process of claim 26, further comprising:

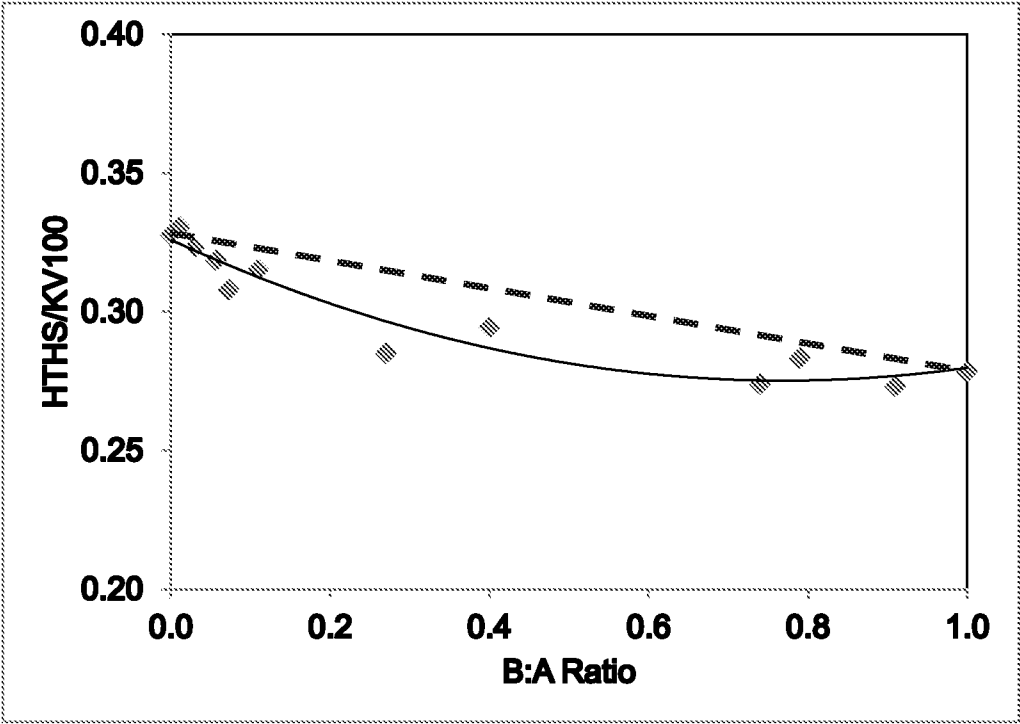
forming the esterified copolymer, comprising:

(1) reacting (i) a vinyl monomer, and (ii) a carboxylic acid monomer comprising an ethylenically unsaturated carboxylic acid or derivative thereof, to form a copolymer;

(2) reacting the copolymer of step (1) with an alcohol or mixture of alcohols under esterifying conditions 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.

Figure 1/1



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055508

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M157/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 2 077 316 A2 (INFINEUM INT LTD [GB]) 8 July 2009 (2009-07-08) paragraphs [0018], [0022] - [0028], [0032] - [0034] paragraphs [0058], [0060]; claims 1,4,5,15,16; examples 1-12 -----	1-28
A	US 6 232 279 B1 (STEIGERWALD EDGAR ANDREAS [DE]) 15 May 2001 (2001-05-15) column 2, line 4 - line 42 column 4, line 14 - line 28; tables 1,2 column 7, line 1 - line 32 -----	1-28
A	US 5 458 792 A (RHODES ROBERT B [US] ET AL) 17 October 1995 (1995-10-17) column 3, lines 49-66; examples 14-26; table 2 ----- -/-	1-28



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/055508

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Information on patent family members

International application No

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