

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 531 176 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

18.05.2005 Bulletin 2005/20

(51) Int Cl.7: **C10M 133/56**, C10M 149/04,
C10M 159/16

(21) Application number: **04256909.5**

(22) Date of filing: **08.11.2004**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LU MC NL PL PT RO SE SI SK TR**

Designated Extension States:

AL HR LT LV MK YU

• **Venhaus, David A.**

Glen Allen, Virginia 23059 (US)

• **Lam, William Y.**

Glen Allen, Virginia 23059 (US)

(30) Priority: **06.11.2003 US 702971**

(71) Applicant: **Afton Chemical Corporation**
Richmond, VA 23219 (US)

(74) Representative: **Cresswell, Thomas Anthony**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(72) Inventors:

• **Loper, John T.**

Richmond, Virginia 23233 (US)

(54) **Hydrocarbyl substituted dispersants and compositions containing the dispersants**

(57) A dispersant for use as a lubricant additive, a lubricant composition and a method for improving engine performance. The dispersant includes at least one member selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines. The hydrocarbyl substituent is composed

of a polymerization product of a raffinate I stream and isobutylene having a number average molecular weight ranging from about 500 to about 3000 as determined by gel permeation chromatography and more than about 70 mol percent of the polymerization product having a terminal vinylidene group.

EP 1 531 176 A2

Description**TECHNICAL FIELD**

[0001] The following disclosure is directed to dispersants for lubricant applications, crankcase dispersants, crankcase lubricant compositions and methods for improving engine performance using novel wear reducing lubricant compositions.

BACKGROUND

[0002] Dispersants are important additives for lubricant compositions. Dispersants maintain impurities and deposits in a suspended state so that they can be removed from the system by filtration or other means rather than being deposited on internal engine components.

[0003] Of the dispersants commonly used in lubricant applications, polymeric Mannich base additives, hydrocarbyl amine adducts, and hydrocarbyl succinic acid derivatives provide exhibit excellent properties for such applications. Mannich base dispersants are typically produced by reacting alkyl-substituted phenols with aldehydes and amines, such as is described in U.S. Pat. Nos. 3,539,633; 3,697,574; 3,704,308; 3,736,535; 3,736,357; 4,334,085; and 5,433,875.

[0004] Hydrocarbyl succinic acid based dispersants are derived by alkylating, for example, maleic anhydride, acid, ester or halide with an olefinic hydrocarbon to form an acylating agent as described in U.S. Patent No. 5,071,919 to DeGonia et al. The acylating agent is then reacted with an amine to form a dispersant. A preferred olefinic hydrocarbon is polyisobutene, also referred to as polyisobutylene.

[0005] Despite the wide variety of dispersants available for lubricant applications, there remains a need for improved dispersants, particularly for crankcase lubricant applications.

SUMMARY OF THE EMBODIMENTS

[0006] In one embodiment herein is presented a dispersant for use as a lubricant additive, a lubricant composition and a method for improving engine performance. The dispersant includes at least one member selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines. The hydrocarbyl substituent is composed of a polymerization product of a raffinate I stream and isobutylene having a number average molecular weight ranging from about 500 to about 3000 as determined by gel permeation chromatography and more than about 70 mol percent of the polymerization product having a terminal vinylidene group.

[0007] In another embodiment there is provided a lubricant additive composed of a first dispersant including at least one member selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines; and a second dispersant including a member selected from the group hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines. The hydrocarbyl substituent of the first dispersant has a number average molecular weight ranging from about 1500 to about 2500 as determined by gel permeation chromatography. The second dispersant has a number average molecular weight ranging from about 500 to about 1200 as determined by gel permeation chromatography.

[0008] In yet another embodiment, a method of reducing engine deposits in an internal combustion engine of a vehicle is provided. The method includes using as a crankcase lubricating oil for the internal combustion engine a lubricant composition containing a lubricant and a lubricant additive. The lubricant additive includes a first dispersant including at least one member selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines; and a second dispersant including a member selected from the group hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines. The hydrocarbyl substituent of the first dispersant has a number average molecular weight ranging from about 1500 to about 2500 as determined by gel permeation chromatography. The second dispersant has a number average molecular weight ranging from about 500 to about 1200 as determined by gel permeation chromatography. The lubricant additive is present in the lubricant composition in an amount sufficient to reduce engine deposits and provide at least a pass rating on an engine deposit test.

[0009] An advantage of the embodiments described herein is that it provides improved dispersants for lubricant compositions, lubricant compositions containing the improved dispersants, and methods for improving engine performance using the improved dispersants. Dispersants in the lubricating oil suspend thermal decomposition and oxidation

products, such as soot and sludge, and reduce or retard the formation of deposits on lubricated surfaces. Dispersants for wear reducing additives are provided by an additive having a hydrocarbyl substituent provided by a polymerization product of a raffinate I stream and isobutene. Such dispersants are effective to meet or exceed GF-4 specifications for passenger car motor oils.

[0010] The dispersant described herein is particularly suitable for crankcase lubricants for diesel and gasoline engines, as a dispersant for automatic transmission fluids, as an additive for continuously variable gear oils, and as a component of hydraulic oils. Other features and advantages of the of the dispersant will be evident by reference to the following detailed description which is intended to exemplify aspects of the preferred embodiments without intending to limit the embodiments described herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] 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 a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) 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 an alicyclic radical);

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

(3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably 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.

[0012] Of the hydrocarbyl substituents, olefinic hydrocarbons are particularly preferred for the hydrocarbyl substituent of at least one dispersant. Olefinic hydrocarbons such as isobutene are typically made by cracking a hydrocarbon stream to produce a hydrocarbon mixture of essentially C₄-hydrocarbons. For example, thermocracking processes (streamcracker) produce C₄ cuts comprising C₄ paraffins and C₄ olefins, with a major component being isobutene. Butadiene and acetylene are substantially removed from the stream by additional selective hydrogenation or extractive distillation techniques. The resulting stream is referred to as "**raffinate I**" and is suitable for polyisobutylene (PIB) synthesis and has essentially the following typical composition: 44-49% of isobutene, 24-28% of 1-butene, 19-21% of 2-butene, 6-8% of n-butane, 2-3% of isobutane. The components of the raffinate I stream may vary depending on operating conditions. Purification of the raffinate I stream provides an essentially pure isobutene product.

[0013] Until now, relatively low molecular weight PIB for use in making dispersants for lubricant and oil compositions has been derived mainly from polymerization of isobutene. The resulting product typically has a vinylidene group content ranging from about 50 to about 60 percent by weight of the polymerization product. The vinylidene group content is believed to have an effect on the reactivity of the PIB during an alkylation process for making a succinic acid adduct, an amine adduct, or an alkyl phenol adduct.

[0014] A hydrocarbyl substituent made from the polymerization of a mixture of raffinate I and isobutene has advantages over polyisobutylene (PIB) derived from isobutene alone. For example, such a hydrocarbyl substituent is relatively more reactive than PIB as evidenced by its vinylidene group content. The vinylidene content of a polymerized mixture of raffinate I and isobutene is typically above about 70% by weight. Also, the polymerized mixture, as described herein, provides a hydrocarbyl polymeric chain including a mixture of gem-dimethyl carbon atoms, methylene carbon atoms, mono-methyl substituted carbon atoms, mono-ethyl substituted carbon atoms. In contrast, polymerization of a relatively pure isobutene reactant provides a mixture of gem-dimethyl carbon atoms and methylene carbon atoms only.

[0015] A preferred polymerization product is provided by polymerizing a mixture of from about 35 to about 45 percent by weight isobutene with from about 55 to about 65 percent by weight raffinate I stream containing at least about 40 % by weight isobutene. The resulting polymerization product has a vinylidene group content of above about 70 percent by weight and preferably, a number average molecular weight ranging from about 500 to about 3000, preferably from about 500 to about 2500 as determined by gel permeation chromatography. Relatively high molecular weight polymerization products have a number average molecular weight ranging from about 1500 to about 2500. Relatively low molecular weight polymerization products have a number average molecular weight ranging from about 500 to about

1200. Both high and low molecular weight polymerization products may be used to make dispersants suitable for lubricant applications.

[0016] The polymerization reaction used to form the polymerization product is generally carried out in the presence of a conventional Ziegler-Natta or metallocene catalyst system. The polymerization medium can include solution, slurry, or gas phase processes, as known to those skilled in the art. When solution polymerization is employed, the solvent may be any suitable inert hydrocarbon solvent that is liquid under reaction conditions for polymerization of alpha-olefins; examples of satisfactory hydrocarbon solvents include straight chain paraffins having from 5 to 8 carbon atoms, with hexane being preferred. Aromatic hydrocarbons, preferably aromatic hydrocarbons having a single benzene nucleus, such as benzene and toluene; and saturated cyclic hydrocarbons having boiling point ranges approximating those of the straight chain paraffinic hydrocarbons and aromatic hydrocarbons described above, are particularly suitable. The solvent selected may be a mixture of one or more of the foregoing hydrocarbons. When slurry polymerization is employed, the liquid phase for polymerization is preferably liquid propylene. It is desirable that the polymerization medium be free of substances that will interfere with the catalyst components.

[0017] Improved dispersant compositions may include dispersants made with the polymerization product described above as the hydrocarbyl group. Other dispersant compositions include at least first and second dispersants each selected from the group consisting of, but not limited to, ashless dispersants such as hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes. The first dispersant preferably has a hydrocarbyl-substituent having a number average molecular weight ranging from about 1500 to about 2500 as determined by gel permeation chromatography, and the second dispersant preferably has a hydrocarbyl-substituent having a number average molecular weight ranging from about 500 to about 1200 as determined by gel permeation chromatography. In a particularly preferred embodiment, the first dispersant is a post treated dispersant and the second dispersant includes a hydrocarbyl-substituent polymerized from a mixture of raffinate I and isobutene as described above.

[0018] Hydrocarbyl-substituted succinic acylating agents are used to make hydrocarbyl-substituted succinimides. The hydrocarbyl-substituted succinic acylating agents include, but are not limited to, hydrocarbyl-substituted succinic acids, hydrocarbyl-substituted succinic anhydrides, the hydrocarbyl-substituted succinic acid halides (especially the acid fluorides and acid chlorides), and the esters of the hydrocarbyl-substituted succinic acids and lower alcohols (e.g., those containing up to 7 carbon atoms), that is, hydrocarbyl-substituted compounds which can function as carboxylic acylating agents. Of these compounds, the hydrocarbyl-substituted succinic acids and the hydrocarbyl-substituted succinic anhydrides and mixtures of such acids and anhydrides are generally preferred, the hydrocarbyl-substituted succinic anhydrides being particularly preferred.

[0019] Hydrocarbyl substituted acylating agents are made by reacting a polyolefin of appropriate molecular weight (with or without chlorine) with maleic anhydride. Similar carboxylic reactants can be used to make the acylating agents. Such reactants include, but are not limited to, maleic acid, fumaric acid, malic acid, tartaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, ethylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic acid, dimethylmaleic acid, hexylmaleic acid, and the like, including the corresponding acid halides and lower aliphatic esters.

[0020] Hydrocarbyl-substituted succinic anhydrides are conventionally prepared by heating a mixture of maleic anhydride and an aliphatic olefin at a temperature of about 175° to about 275° C. The molecular weight of the olefin can vary depending upon the intended use of the substituted succinic anhydrides. Typically, the substituted succinic anhydrides will have a hydrocarbyl group of from 8-500 carbon atoms. However, substituted succinic anhydrides used to make lubricating oil dispersants will typically have a hydrocarbyl group of about 40-500 carbon atoms. Dispersants having a hydrocarbyl group containing from about 8 to about 150 carbon atoms are referred to herein as "relatively low molecular weight dispersants." Whereas dispersants having a hydrocarbyl group containing more than about 150 carbon atoms up to about 500 carbon atoms are referred to herein as "relatively high molecular weight dispersants." With the very high molecular weight substituted succinic anhydrides, it is more accurate to refer to number average molecular weight (M_n) since the olefins used to make these substituted succinic anhydrides may include a mixture of different molecular weight components resulting from the polymerization of low molecular weight olefin monomers such as ethylene, propylene and isobutylene.

[0021] The mole ratio of maleic anhydride to olefin can vary widely. It may vary, for example, from 5:1 to 1:5, a more preferred range is 1:1 to 3:1. With olefins such as polyisobutylene having a number average molecular weight of 500 to 7000, preferably 800 to 3000 or higher and the ethylene-alpha-olefin copolymers, the maleic anhydride is preferably used in stoichiometric excess, e.g. 1.1 to 3 moles maleic anhydride per mole of olefin. The unreacted maleic anhydride can be vaporized from the resultant reaction mixture.

[0022] The hydrocarbyl-substituted succinic anhydrides include polyalkyl or polyalkenyl succinic anhydrides prepared by the reaction of maleic anhydride with the desired polyolefin or chlorinated polyolefin, under reaction conditions well known in the art. For example, such succinic anhydrides may be prepared by the thermal reaction of a polyolefin and maleic anhydride, as described in U.S. Pat. Nos. 3,361,673; 3,676,089; and 5,454,964. Alternatively, the substi-

tuted succinic anhydrides can be prepared by the reaction of chlorinated polyolefins with maleic anhydride, as described, for example, in U.S. Pat. No. 3,172,892. A further discussion of hydrocarbyl-substituted succinic anhydrides can be found, for example, in U.S. Pat. Nos. 4,234,435; 5,620,486 and 5,393,309. Typically, these hydrocarbyl-substituents will contain from 40 to 500 carbon atoms.

[0023] Polyalkenyl succinic anhydrides may be converted to polyalkyl succinic anhydrides by using conventional reducing conditions such as catalytic hydrogenation. For catalytic hydrogenation, a preferred catalyst is palladium on carbon. Likewise, polyalkenyl succinimides may be converted to polyalkyl succinimides using similar reducing conditions.

[0024] The polyalkyl or polyalkenyl substituent on the succinic anhydrides employed herein is generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene and butylene. Preferably, the mono-olefin employed will have 2 to about 24 carbon atoms, and more preferably, about 3 to 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene, 1-octene and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

[0025] Dispersants may be prepared, for example, by reacting the hydrocarbyl-substituted succinic acids or anhydrides with an amine. Preferred amines are selected from polyamines and hydroxyamines. Examples of polyamines that may be used include, but are not limited to, aminoguanidine bicarbonate (AGBC), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA) and heavy polyamines. A heavy polyamine is a mixture of polyalkylenepolyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA but primarily oligomers with 7 or more nitrogen atoms, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures.

[0026] Polyamines that are also suitable in preparing the dispersants described herein include N-arylphenylenediamines, such as N-phenylphenylenediamines, for example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylenediamine, and N-phenyl-1,2-phenylenediamine; aminothiazoles such as aminbthiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole; aminocarbazoles; aminoindoles; aminopyrroles; amino-indazolinones; amino-mercaptotriazoles; aminoperimidines; aminoalkyl imidazoles, such as 1-(2-aminoethyl) imidazole, 1-(3-aminopropyl) imidazole; and aminoalkyl morpholines, such as 4-(3-aminopropyl) morpholine. These polyamines are described in more detail in U.S. Pat. Nos. 4,863,623; and 5,075,383. Such polyamines can provide additional benefits, such as anti-wear and antioxidancy, to the final products.

[0027] Additional polyamines useful in forming the hydrocarbyl-substituted succinimides include polyamines having at least one primary or secondary amino group and at least one tertiary amino group in the molecule as taught in U.S. Pat. Nos. 5,634,951 and 5,725,612. Examples of suitable polyamines include N,N,N',N'-tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N'-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N',N''-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which preferably contain from 1 to 4 carbon atoms each. Most preferably these alkyl groups are methyl and/or ethyl groups. Preferred polyamine reactants of this type include dimethylaminopropylamine (DMAPA) and N-methyl piperazine.

[0028] Hydroxyamines suitable for herein include compounds, oligomers or polymers containing at least one primary or secondary amine capable of reacting with the hydrocarbyl-substituted succinic acid or anhydride. Examples of hydroxyamines suitable for use herein include aminoethylethanolamine (AEEA), aminopropyldiethanolamine (APDEA), ethanolamine, diethanolamine (DEA), partially propoxylated hexamethylene diamine (for example HMDA-2PO or HMDA-3PO), 3-amino-1,2-propanediol, tris(hydroxymethyl)aminomethane, and 2-amino-1,3-propanediol.

[0029] The mol ratio of amine to hydrocarbyl-substituted succinic acid or anhydride preferably ranges from 1:1 to about 2.5:1. A particularly preferred mol ratio of amine to hydrocarbyl-substituted succinic acid or anhydride ranges from about 1.5:1 to about 2.0:1.

[0030] The foregoing dispersant may also be a post-treated dispersant made, for example, by treating the dispersant with maleic anhydride and boric acid as described, for example, in U.S. Patent No. 5,789,353 to Scattergood, or by treating the dispersant with nonylphenol, formaldehyde and glycolic acid as described, for example, in U.S. Patent No. 5,137,980 to DeGonia, et al.

[0031] The Mannich base dispersants are preferably a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). Examples of Mannich condensation products, and methods for their production are described in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536;

3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

[0032] The preferred hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from substantially saturated petroleum fractions and olefin polymers, preferably polymers of mono-olefins having from 2 to about 6 carbon atoms. The hydrocarbon source generally contains at least about 40 and preferably at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a GPC number average molecular weight between about 600 and 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers and polymers made from a mixture of isobutene and a raffinate I stream.

[0033] The preferred Mannich base dispersants are Mannich base ashless dispersants formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to 2.5 moles of formaldehyde and from about 0.5 to 2 moles of polyalkylene polyamine.

[0034] Polymeric polyamine dispersants suitable as the ashless dispersants are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers such as decyl methacrylate, vinyl decyl ether or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300. The preferred polymeric polyamines are hydrocarbyl polyamines wherein the hydrocarbyl group is composed of the polymerization product of isobutene and a raffinate I stream as described above. PIB-amine and PIB-polyamines may also be used.

[0035] Another component of the dispersant compositions according to the embodiments described herein is a multi-functional viscosity index improver such as known in the art and are commercially available. These products and the processes for making them are taught in, for example, U.S. Pat. Nos. 4,732,942; 4,863,623; 5,075,383; 5,112,508; 5,238,588; and 6,107,257, each of which is incorporated herein by reference.

[0036] The multi-function viscosity index improver is preferably a nitrogen containing viscosity index improver. Multi-functional viscosity index improvers include the reaction product of a nitrogen or an oxygen and nitrogen containing ethylenically unsaturated, aliphatic or aromatic monomer grafted on to an olefin copolymer. Suitable nitrogen or oxygen and nitrogen containing ethylenically unsaturated monomers include N-vinyl imidazole, 1-vinyl-2-pyrrolidinone, N-allyl imidazole, allyl amines, 1-vinyl pyrrolidone, 2-vinyl pyridine, 4-vinyl pyridine, N-methyl-N-vinyl acetamide, diallyl formamide, N-methyl-N-allyl formamide, N-ethyl-N-allyl formamide, N-cyclohexyl-N-allyl formamide, 4-methyl-5-vinyl thiazole, N-allyl di-iso-octyl phenothiazine, 2-methyl-1-vinylimidazole, 3-methyl-1-vinylpyrazole, N-vinyl purine, N-vinyl piperazines, N-vinyl succinimide, vinylpiperidines, vinylmorpholines, N-arylphenylenediamines, and mixtures thereof.

[0037] The multi-functional copolymers described above, as well as processes for preparing them, are taught in U.S. Pat. Nos. 4,092,255; 4,170,561; 4,146,489; 4,715,975; 4,769,043; 4,810,754; 5,294,354; 5,523,008; 5,663,126; and 5,814,586; and 6,187,721, each of which is incorporated herein by reference. Of the foregoing, a particularly preferred nitrogen containing viscosity index improver is a reaction product of a maleic anhydride grafted ethylene-propylene copolymer and an N-arylphenylenediamine having a number average molecular weight ranging from about 5,000 to about 50,000. The amount of viscosity index improver in a lubricant composition according to an embodiment ranges from about two to about twelve percent by weight based on the total weight of the lubricant composition.

[0038] Non-dispersant viscosity index improvers may be used in the alternative or in combination with the foregoing nitrogen containing viscosity index improvers. Such non-dispersant viscosity index improvers include, but are not limited to, olefin copolymers, polyalkylmethacrylates, and styrene-maleic esters. Of these, polyalkylmethacrylates are particularly preferred. The viscosity index improver may be supplied in the form of a solution in an inert solvent, typically a mineral oil solvent, which usually is a severely refined mineral oil.

[0039] Suitable materials for use as viscosity index improvers include styrene-maleic esters such as LUBRIZOL® 3702, LUBRIZOL® 3706 and LUBRIZOL® 3715 available from The Lubrizol Corporation; polyalkylmethacrylates such as those available from ROHM GmbH (Darmstadt, Germany) under the trade designations: VISCOPLEX® 5543, VISCOPLEX® 5548, VISCOPLEX® 5549, VISCOPLEX® 5550, VISCOPLEX® 5551 and VISCOPLEX® 5151, from Rohm & Haas Company (Philadelphia, Pa.) under the trade designations ACRYLOID® 1277, ACRYLOID® 1265 and ACRYLOID® 1269, and from Ethyl Corporation (Richmond, Va.) under the trade designation HiTEC® 5710 VII; and olefin copolymer viscosity index improvers such as HiTEC® 5747 VII, HiTEC® 5751 VII, HiTEC® 5770 VII and HiTEC® 5772 VII available from Ethyl Corporation and SHELLVIS® 200 available from Shell Chemical Company. Mixtures of the foregoing products can also be used as well as dispersant and dispersant-antioxidant viscosity index improvers.

[0040] As set forth herein, a dispersant according to the embodiments described herein includes a relatively high or relatively low molecular weight dispersant having a hydrocarbyl group derived from a polymerization product of a raffinate I stream and isobutene or a mixture of a first relatively high molecular weight dispersant and a second relatively low molecular weight dispersant, and optionally a nitrogen-containing viscosity index improver. The first and second

dispersants may be each selected from a hydrocarbyl substituted succinimide, Mannich base dispersant provided by condensing a hydrocarbyl substituted phenol with formaldehyde and a polyalkylene polyamine, and a hydrocarbyl substituted amine. At least one of the first and second dispersants preferably has a number average molecular weight ranging from about 1800 to about 2500, and at least one of the first and second dispersants preferably has a number average molecular weight ranging from about 500 to about 1200 as determined by gel permeation chromatography. Most preferably, at least one of the dispersants contains a hydrocarbyl group derived from a polymerization product of isobutene and a raffinate I stream.

[0041] Mixtures of the first and second dispersants may be made by combining the components in a conventional manner. It is preferred that the higher molecular weight dispersant be present in the mixture in an amount ranging from about 30 to about 70 % by weight, most preferably from about 45 to about 65 % by weight of the total weight of the mixed dispersants. Accordingly, the lower molecular weight dispersant is preferably present in the mixture in an amount ranging from about 70 to about 30% by weight, most preferably from about 35 to about 45 % by weight of the total weight of the mixed dispersants. The total amount of dispersant in a lubricant formulation preferably ranges from about 1 to about 10 % by weight, more preferably from about 3 to about 6 % by weight of the total lubricant formulation weight.

[0042] The following example is given for the purpose of exemplifying aspects of the embodiments and is not intended to limit the embodiments in any way. In the following example, a lubricant containing different dispersant and dispersant mixtures was used and Sequence IIIG engine tests were performed to determine the deposit rating in terms of weighted piston deposit (WPD). The lubricant used for all of the runs was a blend of Group II and Group III lubricating oils, namely 50 wt.% Ultra-S VHV14 Group III from S-Oils, 20 wt.% Conoco 110N Pure-Performance Group II and 30 wt.% Conoco 225N Pure-Performance Group II. The dispersants used in the following example were as follows:

HiTEC® 644 dispersant is a 1000 MW_N PIBSA plus a polyamine.

HiTEC® 646 dispersant is a 1300 MW_N PIBSA plus a polyamine.

HiTEC® 1921 dispersant is a 2100 MW_N PIBSA plus a polyamine post treated with nonylphenol, formaldehyde, and glycolic acid and having a SA/PIB mol ratio of greater than about 1.1.

[0043] All of the foregoing dispersants are available from Ethyl Corporation of Richmond, Virginia. "PIBSA" is defined as polyisobutylene succinic acid or anhydride. The "SA/PIB" ratio is the number of moles of succinic acid or anhydride relative to the number of mols of PIB in the PIBSA adduct.

EXAMPLE 1

[0044]

Sample No.	HiTEC® 1921 (wt.%)	HiTEC® 644 (wt.%)	HiTEC® 646(wt.%)	WPD
1	4.5	----	----	2.50
2	2.5	2.6	----	4.29
3	2.5	----	2.6	2.96
4	3.5	2.0	----	3.70

[0045] As shown by the foregoing example, mixtures of dispersants (Sample Nos. 2, 3, and 4) had a better WPD rating than an oil composition containing a single relatively high molecular weight dispersant (Sample No. 1). The best results, according to the foregoing example, were obtained when a relatively low molecular weight dispersant was mixed with a relatively high molecular weight dispersant (Sample Nos. 2 and 4).

[0046] It is expected that other dispersants available from Ethyl Corporation will perform similarly in dispersant mixtures as described herein. For example, the following dispersants are also available from Ethyl Corporation:

HiTEC® 643 dispersant is a 1300 MW_N PIBSA plus a polyamine wherein the dispersant was post treated with maleic anhydride and boric acid.

HiTEC® 1919 dispersant is a 2100 MW_N PIBSA plus a polyamine post treated with nonylphenol, formaldehyde, and glycolic acid

HiTEC® 1932 dispersant is a 2100 MW_N PIBSA plus a polyamine having a SA/PIB ratio of greater than about 1.1.

HiTEC® 7049 dispersant is a 2100 MW_N PIB-phenol Mannich reaction product.

[0047] Dispersant mixtures may be made as shown in the following table 2 which are merely representative of mix-

tures that may be made and used as described herein and are not intended to limit the embodiments described herein in any way.

Table 2

HiTEC® 1919 (wt.%)	HiTEC® 1921 (wt.%)	HiTEC® 1932 (wt.%)	HiTEC® 644 (wt.%)	PIB-amine 1000 MW _N (wt.%)	PIB-Phenol Mannich 1000 MW _N (wt.%)
3.8	----	----	1.6	----	----
----	3.8	----	----	1.6	----
----	----	3.8	----	----	1.6
3.8	----	----	----	1.6	----
3.8	----	----	----	----	1.6
----	3.8	----	1.6	----	----
----	3.8	----	----	----	1.6
----	----	3.8	1.6	----	----
----	----	3.8	----	1.6	----
1.6	----	----	3.8	----	----
----	1.6	----	----	3.8	----
----	----	1.6	----	----	3.8
1.6	----	----	----	3.8	----
1.6	----	----	----	----	3.8
----	1.6	----	3.8	----	----
----	1.6	----	----	----	3.8
----	----	1.6	3.8	----	----
----	----	1.6	----	3.8	----

[0048] Base oils suitable for use in formulating lubricating oil compositions may be selected from any of the synthetic or natural oils or mixtures thereof. The synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols, poly-alpha-olefins, including polybutenes, alkyl benzenes, organic esters of phosphoric acids, and polysilicone oils. Natural base oils include mineral lubrication oils which may vary widely as to their crude source, e.g., as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. The base oil typically has a viscosity of about 2.5 to about 15 cSt and preferably about 2.5 to about 11 cSt at 100° C.

[0049] The base oil used which may be used to make lubricant compositions as described herein may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

Base Oil Group ¹	Sulfur (wt.%)		Saturates (wt.%)	Viscosity Index
Group I	> 0.03	and/or	< 90	80 to 120
Group II	≤ 0.03	And	≥ 90	80 to 120
Group II	≤ 0.03	And	≥ 90	≥ 120
Group IV	all polyalphaolefins (PAOs)			
Group V	all others not included in Groups I-IV			

¹Groups I-III are mineral oil base stocks.

[0050] The base oil may be selected from a natural oil, synthetic oil or mixture of natural and synthetic oils. Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed par-

affinic-naphthenic types. Oils derived from coal or shale are also suitable. Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0051] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃₋₈ fatty acid esters, or the C₁₃ Oxo acid diester of tetraethylene glycol.

[0052] Another class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0053] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0054] As set forth above, the base oil may be a poly-alpha-olefin (PAO). Typically, the poly-alpha-olefins are derived from monomers having from about 4 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from octene, decene, mixtures thereof, and the like. PAOs may have a viscosity from about 2 to about 15, or from about 3 to about 12, or from about 4 to about 8 cSt at 100° C. Examples of PAOs include 4 cSt at 100° C. poly-alpha-olefins, 6 cSt at 100° C. poly-alpha-olefins, and mixtures thereof. Mixtures of mineral oil with the foregoing poly-alpha-olefins may be used.

[0055] The base oil may be an oil derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons are made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons may be hydroisomerized using the process disclosed in U.S. Pat. Nos. 6,103,099 or 6,180,575; hydrocracked and hydroisomerized using the process disclosed in U.S. Pat. Nos. 4,943,672 or 6,096,940; dewaxed using the process disclosed in U.S. Pat. No. 5,882,505; or hydroisomerized and dewaxed using the process disclosed in U.S. Pat. Nos. 6,013,171, 6,080,301 or 6,165,949.

[0056] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the lubricant base oils. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar

[0057] to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives, contaminants, and oil breakdown products.

[0058] Additives used in formulating the compositions described herein can be blended into the base oil individually or in various sub-combinations. However, it is preferable to blend all of the components concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive concentrate takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also, the use of a concentrate reduces blending time and lessens the possibility of blending errors.

[0059] One embodiment is directed to a method of reducing wear in an internal combustion engine, wherein said method comprises using as the crankcase lubricating oil for said internal combustion engine a lubricating oil containing the dispersant or mixture of dispersants as described herein, wherein the dispersant is present in an amount sufficient to reduce the wear in an internal combustion engine operated using said crankcase lubricating oil, as compared to the wear in said engine operated in the same manner and using the same crankcase lubricating oil except that the oil is

devoid of the dispersant or dispersant mixture. Accordingly, for reducing wear, the dispersant or dispersant mixture is typically present in the lubricating oil in an amount of from 0.1 to 3 weight percent based on the total weight of the oil. Representative of the types of wear that may be reduced using the compositions described herein include cam wear and lifter wear. In other embodiments, the lubricant compositions described herein may be used or formulated as gear oil, hydraulic oils, automatic transmission fluids, and the like.

[0060] At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0061] The foregoing embodiments are susceptible to considerable variation in its practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0062] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

Claims

1. A dispersant for use as a lubricant additive, comprising at least one hydrocarbyl-substituted succinimide, hydrocarbyl-substituted amine or Mannich base adduct derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines, wherein the hydrocarbyl substituent comprises a polymerization product of a raffinate I stream and isobutylene having a number average molecular weight of 500 to 3000 as determined by gel permeation chromatography, and more than 70 mol percent of the polymerization product having a terminal vinylidene group.
2. A dispersant according to claim 1, wherein the polymerization product is derived from a reaction mixture comprising 35 to 45 weight percent isobutylene and 55 to 65 weight percent raffinate I stream.
3. A dispersant according to claim 1 or claim 2, comprising a hydrocarbyl-substituted succinimide derived from the polymerization product and succinic acid, having a ratio of polymerization product to succinic acid of 1.0:1.0 to 1.0:1.6.
4. A dispersant according to claim 1 or claim 2, comprising a Mannich adduct derived from hydrocarbyl-substituted phenols, formaldehydes and polyethylene polyamines.
5. A dispersant according to anyone of the preceding claims, wherein the polymerization product has a number average molecular weight of 500 to 1200 as determined by gel permeation chromatography.
6. A lubricant additive comprising a first dispersant according to any one of claims 1 to 5, and a second dispersant comprising a hydrocarbyl-substituted succinimide, hydrocarbyl-substituted amine or Mannich base adduct derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines.
7. A lubricant additive comprising:
 - a first dispersant comprising at least one hydrocarbyl-substituted succinimide, hydrocarbyl-substituted amine, or Mannich base adduct derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines; and
 - a second dispersant comprising a hydrocarbyl-substituted succinimide, hydrocarbyl-substituted amine or Mannich base adduct derived from hydrocarbyl-substituted phenols condensed with aldehydes and amines,
 wherein the hydrocarbyl substituent of the first dispersant has a number average molecular weight of 1500 to 2500 as determined by gel permeation chromatography and wherein the second dispersant has a number average molecular weight of 500 to 1200 as determined by gel permeation chromatography.
8. A dispersant according to any one of claims 1 to 5, or lubricant additive according to claim 6 or claim 7, further comprising a nitrogen containing viscosity index improver comprising N-vinyl imidazole, 1-vinyl-2-pyrrolidinone, N-allyl imidazole, allyl amines, 1-vinyl pyrrolidone, 2-vinyl pyridine, 4-vinyl pyridine, N-methyl-N-vinyl acetamide, diallyl formamide, N-methyl-N-allyl formamide, N-ethyl-N-allyl formamide, N-cyclohexyl-N-allyl formamide, 4-methyl-5-vinyl thiazole, N-allyl di-iso-octyl phenothiazine, 2-methyl-1-vinylimidazole, 3-methyl-1-vinylpyrazole, N-vinyl

purine, N-vinyl piperazines, N-vinyl succinimide, vinylpiperidines, vinylmorpholines, N-arylphenylenediamines, or mixtures thereof.

- 5 **9.** A dispersant or lubricant additive according to claim 8, wherein the nitrogen containing viscosity index improver comprises a reaction product of a maleic anhydride grafted ethylene-propylene copolymer and an N-arylphenylenediamine, wherein the reaction product has a number average molecular weight of 5,000 to 50,000.
- 10 **10.** A dispersant or lubricant additive according to any one of the preceding claims, further comprising a non-dispersant viscosity index improver comprising an olefin copolymer, polyalkylmethacrylate, or styrene-maleic ester.
- 15 **11.** A lubricant additive according to any one of claims 7 to 10, wherein the hydrocarbyl-substituent of at least one of the first and second dispersants comprises a polymerization product derived from a reaction mixture comprising 35 to 45 weight percent isobutylene and 55 to 65 weight percent raffinate I stream.
- 20 **12.** A lubricant additive according to any one of claims 7 to 11, wherein at least one of the first and second dispersants comprises a hydrocarbyl-substituted succinic acid derivative or a Mannich base adduct derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine.
- 25 **13.** A lubricant additive according to claim 12, wherein the hydrocarbyl-substituted succinic acid derivative or Mannich base adduct derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine comprises a polymerization product derived from a reaction mixture comprising 35 to 45 weight percent isobutylene and 55 to 65 weight percent raffinate I stream.
- 30 **14.** A lubricant additive according to any one of claims 7 to 13, wherein the first dispersant is a post treated dispersant.
- 35 **15.** A lubricant additive according to any one of claims 7 to 14, comprising 30 to 70 percent by weight of the first dispersant and 70 to 30 percent by weight of the second dispersant.
- 40 **16.** A lubricant composition comprising an oil of lubricating viscosity and a dispersant according to any one of claims 1 to 5 or 8 to 10, or a lubricant additive according to any one of claims 6 to 15.
- 45 **17.** A lubricant composition according to claim 16, wherein the dispersant or lubricant additive comprises 0.1 to 10 wt. %, based on the total weight of the lubricant composition.
- 50 **18.** A lubricant composition according to claim 16 or claim 17, wherein the lubricant composition comprises a crankcase oil present in the crankcase of a vehicle, or a drive train lubricant present in an automotive drive train of a vehicle.
- 55 **19.** Use of a lubricant composition according to any one of claims 16 to 18 for lubricating moving parts.
- 60 **20.** Use according to claim 19, wherein the moving parts comprise the moving parts of a vehicle.
- 65 **21.** Use according to claim 20, wherein the moving parts of a vehicle comprise a crankcase or drive train.