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(54) Title: LUBRICATING COMPOSITIONS AND CONCENTRATES CONTAINING AN ANTIWEAR AMOUNT OF A THIA Diazole

(57) Abstract: This invention relates to lubricating compositions comprising a major amount of an oil of lubricating viscosity and at least about 0.4 % by weight of at least one amine free thiazole, wherein the lubricating composition is free of organic polysulfides and contains less than about 2 % by weight of at least one dispersant. The invention also relates to concentrates and methods of using the lubricating compositions to control micro pitting. The lubricants provide improved performance for both macro and micro pitting, especially micro pitting.
LUBRICATING COMPOSITIONS AND CONCENTRATES CONTAINING
AN ANTIWEAR AMOUNT OF A THIADIAZOLE

Field of the Invention

This invention relates to lubricating compositions and concentrates that contains an amine free thiadiazole. The thiadiazole is present to provide improved surface fatigue properties. The lubricants are typically manual transmission fluids and industrial gear oils.

Background of the Invention

Surface fatigue, commonly referred to as pitting or spalling, is a wear mode which results in the loss of material as a result of repeated stress cycles acting on the surface. For years, science has sought to control the large scale wear of equipment with the use of lubricant additives. Additives with active sulfur and phosphorus have been used to control wear. The wear was typically revealed on the surfaces of equipment. Tests were devised to determine the extent of wear protection provided by additives. These test include the 4 ball wear test, the FZG gear test, etc.

There are two major sub-groups under surface fatigue known as micro- and macropitting. As their names imply the type of pitting is related to the size of the pit. Macropits are usually able to be seen with the naked eye as irregular shaped cavities in the surface of the tooth. Damage beginning on the order of 0.5 to 1.0 mm in diameter is considered to be a macropit.

Macropitting is a fatigue phenomenon that can initiate either at or near the surface of a gear tooth. The crack usually propagates for a short distance at a shallow angle to the surface before turning or branching back to the surface. Eventually, the material will dislodge from the surface forming a pit, an irregular shaped cavity in the surface of the material. With gears, the origin of the crack is more likely surface initiated because the lubricant film thickness is low resulting in a high amount of asperity or metal-to-metal contact. For high-speed gears with smooth surface finishes, the film thickness is larger and sub-surface initiated
crack formation may predominate. In these cases an inclusion or small void in the material is a source for stress concentration.

Micropitting is a fatigue phenomenon that occurs in Hertzian contacts that operate in elastohydrodynamic or boundary lubrication regimes and have combined rolling and sliding. Besides operating conditions, such as load, speed, sliding, temperature and specific film thickness, the chemical composition of a lubricant strongly influences micropitting. Damage can start during the first $10^5$ to $10^6$ stress cycles with generation of numerous surface cracks. The cracks grow at a shallow angle to the surface forming micropits that are about 10–20 μm deep by about 25-100 μm long and 10–20 μm wide. The micropits appear as a dull, matte surface to the observer.

Micropitting is the preferred name for this mode of damage, but it has also been referred to as grey staining, grey flecking, frosting and peeling. Although micropitting generally occurs with heavily loaded, carburized gears, it also occurs with nitrided, induction hardened and through-hardened gears. Micropitting may arrest after running-in. If micropitting continues to progress, however, it may result in reduced gear tooth accuracy, increased dynamic loads and noise. Eventually, it can progress to macropitting and gear failure.

It is desirable to have a lubricant which provide improved wear protection, especially improved protection from micropitting.

**Summary of the Invention**

This invention relates to lubricating compositions comprising a major amount of an oil of lubricating viscosity and at least about 0.4% of at least one amine free thiazolizole, wherein the lubricant is free of organic polysulfides and contains less than about 2% by weight of at least one dispersant. The invention also relates to concentrates and methods of using the lubricating compositions to control surface fatigue. The lubricants provide improved performance for surface fatigue.

**Detailed Description of the Preferred Embodiments**

The term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. Substantially hydrocarbon describes groups which contain heteroatom substituents which do not alter the predominantly hydrocarbon nature of the group. Examples of hydrocarbyl groups include the following:
(1) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, sulfoxyl, etc.);

(3) heteroatom substituents, i.e., substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc.

In general, no more than about 2, or no more than one, hetero substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such hetero atom substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

The term "organinc polysulifde" refers to organic compounds which contain sulfide linkages of two or more sulfur atoms. The sulfide linkages usually extend between two or more unsaturated compounds, such as olefins. These organic polysulfides have been referred to as polysulfurized olefins which are illustrated by the reaction of olefins with sulfur, sulfur compounds or a combination thereof to form a reaction product that contains an average of more than one sulfur atom per olefins. These products are generally referred to as polysulfurized olefins or polysulfides. An example of these products is the reaction product of isobutylene, sulfur and hydrogen sulfide under pressure.

In the specification and claims, the term "lubricating composition" refers to the combination of an oil of lubricating viscosity and additives. The percentages
by weight are based on the total amount of the additive and the oil of lubricating viscosity. If not specifically stated, the oil of lubricating viscosity makes up the balance of the lubricating composition.

As described herein, the lubricating compositions contain less than about 2% by weight of at least one dispersant. When dispersant levels exceed about 2% by weight, the lubricating compositions are more susceptible to foaming. The foaming destroys the lubricants ability to form a protective layer over the surface of the equipment, such as the gears and pinions of a manual transmission or industrial gear assembly. In one embodiment, the dispersant is present in an amount less than about 1.5%, or less than about 1% by weight. In another embodiment, the lubricating compositions is free of one or all of the dispersants described below. In another embodiment the lubricating composition is free of dispersants.

As described above, the lubricating compositions contain at least about 0.4% of at least one amine free thiadiazole. These thiadiazoles are typically oil soluble or oil dispersible. The term "amine free" refers to thiadiazole derivatives which are not prepared using amines. Amine-free thiadiazole are those that are not amine salts or amine coupled thiadiazoles when added to the lubricating oil. The present amine free thiadiazoles derivatives are not prepared using an amine. In one embodiment, the lubricating compositions contain at least about 0.6%, or at least about 0.8% or at least about 0.9% by weight of at least one thiadiazole compound. In one embodiment, the lubricating composition contains up to about 8%, or up to about 5%, or up to about 3% by weight of at least one thiadiazole compound. In another embodiment, thiadiazole provides the only sulfur from additives to the lubricating composition. It should be noted that the oils of lubricating viscosity may contain sulfur inherently.

The present invention involves derivatives of thiadiazoles. Thiadiazoles, which are cyclic compounds in which the ring contains 2 nitrogen, 2 carbon, and 1 sulfur atoms. They are discussed by W. R. Sherman, "The Thiadiazoles," in Heterocyclic Compounds, Volume 7, R. C. Elderfield Editor, John Wiley & Sons, Inc. New York, Pages 541-626, 1961. The synthesis and properties of many thiadiazoles are described in this reference. Examples of thiadiazoles include 2,5-substituted-1,3,4-thiadiazole; 3,5-substituted-1,2,4-thiadiazole; 3,4-
substituted-1,2,5-thiadiazole; and 4,5-substituted-1,2,3-thiadiazole. The compound which is most readily available and particularly useful for purposes of the present invention, is 2,5-substituted-1,3,4-thiadiazole, of which an example is 2,5-dimercapto-1,3,4-thiadiazole, sometimes referred to herein as "DMTD." It should be understood, however, that the term DMTD, as used herein, can encompass any of the dimercaptothiadiazoles or mixtures of two or more dimercaptothiadiazoles. A convenient preparation of 2,5-dimercapto-1,3,4-thiadiazole is the reaction of 1 mole of hydrazine or a salt of hydrazine with 2 moles of carbon disulfide in an alkaline medium. The product can be recovered by acidification of the reaction mixture.

The thiadiazole derivatives include a) mono or di substituted hydrocarbylthio or hydrocarbyldithio substituted thiadiazoles; b) carboxylic esters of DMTD; c) condensation products of halogenated aliphatic monocarboxylic acids with DMTD; d) reaction products of unsaturated cyclic hydrocarbons and unsaturated ketones with DMTD; e) reaction products of an aldehyde, and an alcohol or aromatic hydroxy compound, and DMTD; f) reaction products of an aldehyde, a mercaptan and DMTD; and g) mixtures of two or more thereof. Compositions a-g are described in U.S. Patent 4,612,129 and patent references cited therein. This patent is hereby incorporated by reference.

In one embodiment, the thiadiazole derivatives include mono or disubstituted thiadiazoles having a hydrocarbylthio group, a hydrocarbyldithio group, or mixture of these groups. Examples of these thiadiazoles include hydrocarbylthio, mercaptothiadiazole; bis-(hydrocarbylthio) thiadiazole; hydrocarbyldithio, mercaptothiadiazole; and bis-(hydrocarbyldithio) thiadiazole.

It is understood that the hydrocarbyl groups on the thiadiazole may be the same or different. The hydrocarbyl groups may be aliphatic or aromatic, including alkyl, cyclic, alicyclic, aralkyl, aryl and alkaryl. In one embodiment, the hydrocarbyl groups independently contain from 1 to about 30, or from about 2 to about 24, or from about 4 to about 12 carbon atoms. Here and elsewhere in the specification and claims, the range or ratio limits may be combined. Examples of specific hydrocarbyl groups may be an alkyl group such as methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, nonyl, decyl or dodecyl groups undecyl, dodecyl, cetyl goups, and isomers thereof.
The 1,3,4-thiadiazole compounds, or mixtures thereof, contemplated for use in the present invention can be readily obtained from commercial sources, such as the Amoco Petroleum Additives Company, or can be synthesized from hydrazine and carbon disulfide in a well-known manner. Particularly useful thiadiazoles include compositions commercially available from the Amoco Petroleum Additives Company under the trade names "Amoco-153" and "Amoco-158". A 2,5-bis-(hydrocarbyldithio)-1,3,4-thiadiazole and its monosubstituted equivalent 2-hydrocarbylthio-5-mercapto-1,3,4-thiadiazole are commercially available as a mixture of the two compounds in a ratio of about 85 percent bis-hydrocarbyl to 15 percent monohydrocarbyl from the Ethyl Corporation as Hitec 4313. U.S. Patents 2,719,125; 2,719,126; 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,087,937; 3,663,561; 3,862,798; and 3,840,549 may be referred to for detailed procedures on the preparation of the 1,3,4-thiadiazole compounds contemplated for use in lubricating compositions of the present invention. These patents are incorporated by reference herein.

A process for preparing such derivatives is described in U.S. Patent 2,191,125 as comprising the reaction of DMTD with a suitable sulfenyl chloride or by reacting the dimercapto diathiazole with chlorine and reacting the resulting disulfenyl chloride with a primary or tertiary mercaptan. Suitable sulfenyl chlorides useful in the first procedure can be obtained by chlorinating a mercaptan (RSH or R¹ SH) with chlorine in carbon tetrachloride. In a second procedure, DMTD is chlorinated to form the desired bisulfenyl chloride which is then reacted with at least one mercaptan (RSH and/or R¹ SH). The disclosures of U.S. Patents 2,719,125; 2,719,126; and 3,087,937 are hereby incorporated by reference for their description of derivatives of DMTD useful in the compositions of the invention. U.S. Patent 3,087,932 describes a one-step process for preparing 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazole. The procedure involves the reaction of either DMTD or its alkali metal or ammonium salt and a mercaptan in the presence of hydrogen peroxide and a solvent.

Oil-soluble or oil-dispersible reaction products of DMTD can be prepared also by the reaction of the DMTD with a mercaptan and formic acid. Compositions prepared in this manner are described in U.S. Patent 2,749,311.
Any mercaptan can be employed in the reaction, such as aliphatic and aromatic mono- or poly-mercaptan containing from 1 to about 30, or from about 2 to about 18, carbon atoms. The disclosures of U.S. Patents 3,087,932 and 2,749,311 are hereby incorporated by reference for their description of DMTD derivatives which can be utilized as components of the composition of this invention. It will be understood by those skilled in the art that the reactions outlined above produce some amounts of the monohydrocarbyldithio-thiadiazole as well as the bis-hydrocarbyl compounds. The ratio of the two can be adjusted by varying the amounts of the reactants.

The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles is described in U.S. Patent 3,663,561, which is hereby incorporated by reference. The compositions are prepared by the oxidative coupling of equimolecular portions of a hydrocarbyl mercaptan and DMTD or its alkali metal mercaptide. The mono-mercaptans used in the preparation of the compounds are represented by the formula R¹ SH, wherein R¹ is a hydrocarbyl group containing from 1 to about 28 carbon atoms. A peroxo compound, hypohalide or air, or mixtures thereof can be utilized to promote the oxidative coupling. Specific examples of the mono-mercaptan include methyl mercaptan, isopropyl mercaptan, hexyl mercaptan, decyl mercaptan, and long chain alkyl mercaptans, for example, mercaptans derived from the polyalkenes described herein, such as propene polymers and isobutylene polymers especially polyisobutylene, having 3 to about 70 propene or isobutylene units per molecule. The disclosure of U.S. Patent 3,663,561 is hereby incorporated by reference for its identification of DMTD derivatives, which are useful as components in the compositions of this invention.

Carboxylic esters of DMTD (b) are described in U.S. Patent 2,760,933. These esters are prepared by reacting DMTD with an organic acid halide (chloride) and a molar ratio of 1:2 at a temperature of from about 25 to about 130°C. Suitable solvents, such as benzene or dioxane, can be utilized to facilitate the reaction. The reaction product is washed with dilute aqueous alkali to remove hydrogen chloride and any unreacted carboxylic acid. The disclosure of U.S. Patent 2,760,933 is hereby incorporated by reference for its description.
of various DMTD derivatives which can be utilized in the compositions of the present invention.

Condensation products of alpha-halogenated aliphatic monocarboxylic acids with DMTD (c) are described in U.S. Patent 2,836,564. Examples of alpha-halogenated aliphatic fatty acids which can be used include alpha-bromo or alpha-chloro carboxylic acids containing form about 6 to about 30, or from about 8 to about 24 carbon atoms. Specific examples include alpha-bromo-lauric acid, alpha-chloro-lauric acid, alpha-chloro-stearic acid, etc. The disclosure of U.S. Patent 2,836,564 is hereby incorporated by reference for its disclosure of derivatives of DMTD which can be utilized in the compositions of the present invention.

Oil-soluble reaction products of unsaturated cyclic hydrocarbons and unsaturated ketones (d) are described in U.S. Patents 2,764,547 and 2,799,652, respectively, and a disclosure of these references also are hereby incorporated by reference for their description of materials. Examples of unsaturated cyclic hydrocarbons described in the '547 patent include styrene, alpha-methyl styrene, pinene, dipentene, cyclopentadiene, etc. The unsaturated ketones, described in U.S. Patent 2,799,652, include aliphatic, aromatic or heterocyclic unsaturated ketones containing from about 4 to about 40 carbon atoms and from 1 to 6 double bonds. Examples include mesityl oxide, phorone, isophorone, benzal acetophenone, furfural acetone, difurfuryl acetone, etc.

U.S. Patent 2,850,453 describes products which are obtained by reacting DMTD, an aldehyde and an alcohol or an aromatic hydroxy compound (e) in a molar ratio of from 1:2:1 to 1:6:5. The aldehyde employed can be an aliphatic aldehyde containing from 1 to about 20 carbon atoms or an aromatic or heterocyclic aldehyde containing from about 5 to about 30 carbon atoms. Examples of suitable aldehydes include formaldehyde, acetaldehyde, benzaldehyde, etc. The reaction can be conducted in the presence or absence of suitable solvents by (a) mixing all of the reactants together and heating, (b) by first reacting an aldehyde with the alcohol or the aromatic hydroxy compound, and then reacting the resultant intermediate with the thiadiazole, or (c) by reacting the aldehyde with thiadiazole first and the resulting intermediate with the
hydroxy compound. The disclosure of U.S. Patent 2,850,453 is hereby incorporated by reference.

U.S. Patent 2,703,784 describes products obtained by reacting DMTD with an aldehyde and a mercaptan (f). The aldehydes are similar to those disclosed in U.S. Patent 2,850,453. The disclosure of this patent also is incorporated by reference. The mercaptans may be one or more of those described herein. In one embodiment, the mercaptans are aliphatic or aromatic mono- or poly-mercaptans containing from about 1 to about 30, or from about 2 to about 24 carbon atoms. Examples of suitable mercaptans include ethyl mercaptan, butyl mercaptan, octyl mercaptan, etc.

U.S. Patent 3,663,561 describes thiadiazole derivatives which are prepared by the oxidative coupling of equimolecular portions of a hydrocarbyl mercaptan and DMTD or its alkali metal mercaptide. The mono-mercaptans used in the preparation of the compounds include those described herein and may be represented by the formula R'SH, wherein R' is a hydrocarbyl group containing from 1 to about 280 carbon atoms. A peroxo compound (such as the peroxides described herein) hypohalide or air, or mixtures thereof can be utilized to promote the oxidative coupling. Specific examples of the mono-mercaptan include methyl mercaptan, isopropyl mercaptan, hexyl mercaptan, decyl mercaptan, and long chain alkyl mercaptans, for example, mercaptans derived from propene polymers and isobutylene polymers especially polyisobutylenees, having 3 to about 70 propene or isobutylene units per molecule. The disclosure of U.S. Patent 3,663,561 is hereby incorporated by reference.

**Dispersants**

The lubricating compositions may also contain at least one dispersant. In one embodiment, the dispersants are selected from (a) acylated nitrogen dispersants, (b) hydrocarbyl substituted amines, (c) carboxylic ester dispersants, (d) Mannich dispersants, and (e) mixtures thereof. The dispersant are generally present in an amount from about 0.1% to about 2%, or from about 0.2% to about 1.75%, or from about 0.3% to about 1.4% by weight. In one embodiment, the dispersants are present in an amount of less than 2%, or less than 1.5%, or less than 1% by weight.
The acylated nitrogen dispersants include reaction products of one or more carboxylic acylating agents such as the hydrocarbyl-substituted carboxylic acylating agents and an amine. In one embodiment, the hydrocarbyl groups are derived from one or more of polyalkenes. The polyalkene includes homopolymers and inter polymers of olefins having from 2 to about 40, or from 3 to about 24, or from 4 to about 12 carbon atoms. The olefins may be monoolefins, such as ethylene, propylene, 1-butene, isobutene, an alpha-olefin, or polyolefinic monomers, including diolefinic monomers, such 1,3-butadiene and isoprene. The alpha-olefins generally have from about 4 to about 30, or from about 8 to about 18 carbon atoms. These olefins are sometimes referred to as mono-1-olefins or terminal olefins. The "-olefins and isomerized "-olefins include 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tetraicosene, etc. Commercially available "-olefin fractions that can be used include the C_{15-18} olefins, C_{12-16} -olefins, C_{14-16} -olefins, C_{14-18} olefins, C_{16-18} -olefins, C_{18-20} -olefins, C_{18-24} -olefins, C_{22-28} -olefins, etc. The polyalkenes are prepared by conventional procedures. The polyalkenes are described in U.S. Patent 3,219,666 and 4,234,435, the disclosures of which is hereby incorporated by reference. Examples of polyalkenes includes polypropylenes, polybutylenes, polyisoprene and polybutadienes. In one embodiment, the polyalkene is a homopolymer, such as a polybutene. One example of a useful polybutene is a polymer where about 50% of the polymer is derived from isobutylene. Useful polybutenes include those having an Mw of about 4,000 to about 8,000, or 6,000 to about 7,000.

In one embodiment, the polyalkene is derived from one or more dienes. The dienes include 1,3 pentadiene, isoprene, methylisoprene, 1,4-hexadiene, 1,5-heptadiene, 1,6-octadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, linear 1,3-conjugated dienes (e.g. 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 1,3-hexadiene) and cyclic dienes (e.g. cyclopentadiene, dicyclopentadiene, fulvene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene, and cyclooctatetraene). The polyalkene may be a homopolymer of a diene, or a co- or terpolymer of a diene with either another diene or one or more of the above monoolefins. The polyalkene may be hydrogenated. A commercially available
polyalkene derived from at least one diene is LIR-290, a hydrogenated polyisoprene (Mw=25,000), available commercially from Kuraray Co, Ltd.

The polyalkene is generally, characterized as containing from at least about 8 carbon atoms up to about 300, or from about 30 up to about 200, or from about 35 up to about 100 carbon atoms. In one embodiment, the polyalkene is characterized by an Mn (number average molecular weight) greater than about 400, or greater than about 500. Generally, the polyalkene is characterized by an Mn from about 500 up to about 5000, or from about 700 up to about 2500, or from about 800 up to about 2000, or from about 900 up to about 1500. In another embodiment, the polyalkene has a Mn up to about 1300, or up to about 1200.

Number average molecular weight, as well as weight average molecular weight and the entire molecular weight distribution of the polymers, are provided by gel permeation chromatography (GPC). For purpose of this invention a series of fractionated polyisobutene, is used as the calibration standard in the GPC. The techniques for determining Mn and Mw values of polymers are well known and are described in numerous books and articles. For example, methods for the determination of Mn and molecular weight distribution of polymers is described in W.W. Yan, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs", J. Wiley & Sons, Inc., 1979.

In another embodiment, the polyalkenes have a Mn from about 1300 up to about 5000, or from about 1500 up to about 4500, or from about 1700 up to about 3000. The polyalkenes also generally have a Mw/Mn from about 1.5 to about 4, or from about 1.8 to about 3.6, or from about 2.5 to about 3.2. The hydrocarbaryl substituted carboxylic acalyting agents are described in U.S. Patent 4,234,435, the disclosure of which is hereby incorporated by reference.

In another embodiment, the acylating agents are prepared by reacting one or more of polyalkene with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group, i.e., polyalkenyl group, is at least 1.3. The maximum number will generally not exceed 4.5. A suitable range is from about 1.4 to 3.5 and or from about 1.4 to about 2.5 succinic groups per equivalent weight of substituent groups.
The above-described carboxylic acylating agents are reacted with one or more amines to form the acylated nitrogen dispersants. The amines may be mono or polyamines, or mixture of mono and polyamines. The amines may be primary amines, secondary amines or tertiary amines. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference.

The monoamines generally contain from 1 up to about 24 carbon atoms, or up to about 12, or up to about 6 carbon atoms. Examples of monoamines include methylamine, ethylamine, propylamine, butylamine, octylamine, and dodecylamine, dimethylamine, diethyamine, dipropylamine, dibutylamine, methyl butylamine, ethyl hexylamine, trimethylamine, tributylamine, methyl diethyamine, ethyl dibutylamine, etc.

In one embodiment, the amine may be a fatty (C_{4-30}) amine which include n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleylamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Armak Chemicals, Chicago, Illinois), such as Armak's Armeen-C, Armeen-O, Armeen-OL, Armeen-T, Armeen-HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or soya groups.

Other useful amines include primary ether amines, such as those represented by the formula, R^\text{\textprime} \text{(ORN)}_x \text{NH}_2, wherein RN is a divalent alkylene group having about 2 to about 6 carbon atoms, x is a number from one to about 150 (or one), and R^\text{\textprime} is a hydrocarbyl group of about 5 to about 150 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Useful etheramines are exemplified by those identified as SURFAM P14B (decylxypropylamine), SURFAM P16A (linear C_{16}), SURFAM P17B (tridecylxypropylamine). The carbon chain lengths (i.e., C_{14}, etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In one embodiment, the amine may be a hydroxyamine. Typically, the hydroxyamines are primary, secondary or tertiary alkanol amines or mixtures
thereof. Such amines can be represented by the formulae: $H_2NHR'OH$, 
$H(R'_1)NR'R'OH$, and $(R'_1)_2NHR'OH$, wherein each $R'_1$ is independently a 
hydrocarbyl group having from one to about eight carbon atoms or 
hydroxyhydrocarbyl group having from one to about eight carbon atoms, or from 
one to about four, and $R'$ is a divalent hydrocarbyl group offrom about two to 
about 18 carbon atoms, or from two to about four. The group $-R'-OH$ in such 
formulae represents the hydroxyhydrocarbyl group. $R'$ can be an acyclic, 
alicyclic or aromatic group. Typically, $R'$ is an acyclic straight or branched 
alkylene group, such as an ethylene, propylene, 1,2-butylene, 1,2-octadecylene, 
etc. group. Where two $R'1$ groups are present in the same molecule they can be 
joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, 
nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of 
such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, - 
thiomorpholines, -piperidines, --oxazolidines, -thiazolidines and the like.

Typically, however, each $R'_1$ is independently a methyl, ethyl, propyl, butyl, 
pentyl or hexyl group. Examples of these alkanolamines include mono-, di-, and 
triethanolamine, diethylethanolamine, ethylethanolamine, butyldiethanolamine, 
etc.

The hydroxyamines may also be an ether N-(hydroxyhydrocarbyl)amine.

These are hydroxypoly(hydrocarbyloxy) analogs of the above-described 
hydroxyamines (these analogs also include hydroxyl-substituted oxyalkylene 
analogs). Such N-(hydroxyhydrocarbyl) amines can be conveniently prepared 
by reaction of one or more of the above epoxides with afore described amines 
and may be represented by the formulae: $H_2N(R'O)_{2x}H$, $H(R'_1)N(R'O)_{2x}H$, and 
$(R'_1)_2N(R'O)_{2x}H$, wherein $x$ is a number from about 2 to about 15 and $R_1$ and $R'$ 
are as described above. $R'_1$ may also be a hydroxypoly(hydrocarbyloxy) group.

The amines may be hydroxyamines, such as those represented by the 
formula $R_1 - (N - (R_2O)_aH) - (R_3)_a - (N - (R_2O)_aH) - (R_2O)_aH$, wherein $R_1$ is a 
hydrocarbyl group generally containing from about 6 to about 30 carbon atoms; 
$R_2$ and each $R_3$ is independently an alkylene group containing up to about 5 
carbon atoms, or an ethylene or propylene group; $a$ is zero or one; and each $z$ is 
independently a number from zero to about 10, with the proviso that at least one 
z is at least one. These hydroxyamines can be prepared by techniques well
known in the art and many such hydroxyamines are commercially available. The hydroxy amines include mixtures of amines such as obtained by the hydrolysis of fatty oils (e.g., tallow oils, sperm oils, coconut oils, etc.). Specific examples of fatty amines, containing from about 6 to about 30 carbon atoms, include saturated as well as unsaturated aliphatic amines, such as octyl amine, decyl amine, lauryl amine, stearyl amine, oleyl amine, dodecyl amine, and octadecyl amine.

Useful hydroxyamines wherein a in the above formula is zero include 2-hydroxyethyl, hexylamine; 2-hydroxyethylectylamine; 2-hydroxyethyl, pentadecylamine; 2-hydroxyethyl, oleylamine; 2-hydroxyethyl,soyamine; bis(2-hydroxyethyl) hexylamine; bis(2-hydroxyethyl) oleylamine; and mixtures thereof. Also included are the comparable members wherein in the above formula at least one of z is at least 2, as for example, 2-hydroxyethoxyethyl, hexylamine.

A number of hydroxyamines wherein a in the above formula is zero are available from the Armak Chemical Division of Akznova, Inc., Chicago, Illinois, under the general trade designations "Ethomeen" and "Propomeen". Specific examples of such products include: Ethomeen C/15 which is an ethylene oxide condensate of a coco alkyl amine containing about 5 moles of ethylene oxide; Ethomeen C/20 and C/25 which are ethylene oxide condensation products from coco alkyl amine containing about 10 and 15 moles of ethylene oxide, respectively; Ethomeen O/12 which is an ethylene oxide condensation product of oleylamine containing about 2 moles of ethylene oxide per mole of amine; Ethomeen S/15 and S/20 which are ethylene oxide condensation products with stearyl amine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; Ethomeen T/12, T/15 and T/25 which are ethylene oxide condensation products of tallow amine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively; and Propomeen O/12 which is the condensation product of one mole of oleylamine with 2 moles propylene oxide.

Commercially available examples of alkoxylated amines where a in the above formula is one include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallow trimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.
The amine may also be a polyamine. The polyamines include alkoxyalted diamines, fatty diamines, alkylene polyamines, hydroxy containing polyamines, condensed polyamines and heterocyclic polyamines. Commercially available examples of alkoxyalted diamines include those amines where a in the above formula is one. Examples of these amines include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallowtrimethylene diamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

In another embodiment, the polyamine is a fatty diamine. The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylenediamines, propanediamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Armak Chemical Co., Chicago, Illinois.

In another embodiment, the amine is an alkylene polyamine. Alkylene polyamines are represented by the formula HR₁N-(Alkylene-N)ᵦ(R₁)₂, wherein each R₁ is independently hydrogen; or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms; n is a number from 1 to about 10, or from about 2 to about 7, or from about 2 to about 5; and the "Alkylene" group has from 1 to about 10 carbon atoms, or from about 2 to about 6, or from about 2 to about 4. In another embodiment, R₁ is defined the same as R₁ above. Such alkylene polyamines include methylene polyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripopylenetetramine, triethylenetetramine, tetraethylenepentamine, hexaethylenepentamine, pentaethylenetetramine, etc.

Higher homologs obtained by condensing two or more of the above-noted alkyleneamines are similarly useful as are mixtures of two or more of the afore described polyamines.
In one embodiment, the polyamine is an ethylenepolyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamines are often a complex mixture of polyalkylenepolyamines including cyclic condensation products. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". In general, alkylenepolyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200 °C.

A typical sample of such ethylenepolyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a specific gravity at 15.6 °C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40 °C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72% triethylenetetraamine, 21.74% tetraethylenepentamine and 76.61% pentaethylenhexamine and higher analogs. These alkylenepolyamine bottoms include cyclic condensation products, such as piperazine, and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms may be reacted solely with the acylating agent or they may be used with other amines, polyamines, or mixtures thereof.

Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are polyhydric alcohols or polyhydric amines. The polyhydric alcohols are described below. In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20, or from two to about eight carbon atoms. Examples of polyhydric amines include tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetrakis (2-hydroxyethyl) ethylenediamine, or tris(hydroxymethyl) aminomethane (THAM).
Polyamines which may react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Useful polyamines include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms". The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually from about 60 °C to about 265 °C, or from about 220 °C to about 250 °C in the presence of an acid catalyst.

The amine condensates and methods of making the same are described in PCT publication WO 86/05501 and U.S. Patent 5,230,714 (Steckel) which are incorporated by reference for its disclosure to the condensates and methods of making. A particularly useful amine condensate is prepared from HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1% by weight nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), and tris(hydroxymethyl)aminomethane (THAM).

In another embodiment, the polyamines are polyoxyalkylene polyamines, e.g. polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, or from about 400 to about 2000. Useful polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc.". U.S. Patents 3,804,763 and 3,948,800 are expressly incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines and acylated products made therefrom.

In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxy monoamines, particularly alkoxyluted alkylene polyamines, e.g., N,N(diethanol)ethylene diamines may also be used. Such polyamines can be made by reacting one or more above-described alkylene amines with one or more of the above-described alkylene oxides. Similar alkylene oxide-alkanol amine reaction products may
also be used such as the products made by reacting the above described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1.1 to 1.2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art. Specific examples of hydroxy-containing polyamines include N-(2-hydroxyethyl) ethylenediamine, N,N'-bis(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl)piperazine, mono(hydroxypropyl)-substituted tetaethylenepentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the above described polyamines are also useful.

In another embodiment, the amine is a heterocyclic amine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminomethylmorpholines, N-aminoalkylthiomorpholines, N-aminomethylpiperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Useful heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially useful. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring.

Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminomethylpiperazine, and N,N'-diaminoethyipiperazine. Hydroxy heterocyclic amines are also useful. Examples
include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

Acylated nitrogen dispersants and methods for preparing the same are described in U.S. Patents 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; and 4,904,401. The disclosures of acylated nitrogen dispersants and other dispersants contained in those patents is hereby incorporated by reference.

The dispersant may also be a hydrocarbyl-substituted amines. These hydrocarbyl-substituted amines are well known to those skilled in the art. These amines are disclosed in U.S. Patents 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433; and 3,822,289. These patents are hereby incorporated by reference for their disclosure of hydrocarbyl amines and methods of making the same.

Typically, hydrocarbyl substituted amines are prepared by reacting olefins and olefin polymers (polyalkenes) with amines (mono- or polyamines). The polyalkene may be any of the polyalkenes described above. The amines may be any of the amines described above. Examples of hydrocarbyl substituted amines include poly(propylene)amine; N,N-dimethyl-N-poly(ethylene/propylene)amine, (50:50 mole ratio of monomers); polybutene amine; N,N-di(hydroxyethyl)-N-polybutene amine; N-(2-hydroxypropyl)-N-polybutene amine; N-polybutene-aniline; N-polybutenemorpholine; – poly(butene)ethylenediamine; –poly(propylene)trimethylenediamine; – poly(butene)diethylenetriamine; N',N'-poly(butene)tetraethylenepentamine; N,N-dimethyl-N'-poly(propylene)-1,3-propylenediamine and the like.

In another embodiment, the dispersant may also be a carboxylic ester dispersant. The carboxylic ester dispersant is prepared by reacting at least one of the above hydrocarbyl-substituted carboxylic acylating agents with at least one organic hydroxy compound and optionally an amine. In another embodiment, the carboxylic ester dispersant is prepared by reacting the acylating agent with at least one of the above-described hydroxyamines.

The organic hydroxy compound includes compounds of the general formula R""(OH)m wherein R" is a monovalent or polyvalent organic group joined to the -OH groups through a carbon bond, and m is an integer of from 1 to about
10 wherein the hydrocarbyl group contains at least about 8 aliphatic carbon atoms. The hydroxy compounds may be aliphatic compounds, such as monohydric and polyhydric alcohols, or aromatic compounds, such as phenols and naphthols. The aromatic hydroxy compounds from which the esters may be derived are illustrated by the following specific examples: phenol, beta-naphthol, alpha-naphthol, cresol, resorcinol, catechol, \( p,p' \)-dihydroxybiphenyl, 2-chlorophenol, 2,4-dibutylyphenol, etc.

The alcohols from which the esters may be derived generally contain up to about 40 aliphatic carbon atoms, or from 2 to about 30, or from 2 to about 10. They may be monohydric alcohols such as methanol, ethanol, isooctanol, dodecanol, cyclohexanol, etc. In one embodiment, the hydroxy compounds are polyhydric alcohols, such as alkyene polyols. In one embodiment, the polyhydric alcohols contain from 2 to about 40 carbon atoms, or from 2 to about 20; and or from 2 to about 10 hydroxyl groups, or from 2 to about 6. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butane diol; hexane diol; sorbitol; arabinol; mannitol; sucrose; fructose; glucose; cyclohexane diol; erythritol; and pentaerythritols, including di- and tripentaerythritol. Particularly useful polyhydric alcohols include diethylene glycol, triethylene glycol, glycerol, sorbitol, pentaerythritol and dipentaerythritol.

The polyhydric alcohols may be esterified with monocarboxylic acids having from 2 to about 30 carbon atoms, or from about 8 to about 18, provided that at least one hydroxyl group remains unesterified. Examples of monocarboxylic acids include acetic, propionic, butyric and fatty carboxylic acids.

The fatty monocarboxylic acids are described above. Specific examples of these esterified polyhydric alcohols include sorbitol oleate, including mono- and dioleate, sorbitol stearate, including mono- and distearate, glycerol oleate, including glycerol mono- and di- and trioleate and erythritol octanoate.

The carboxylic ester dispersants may be prepared by any of several known methods. The method which is particularly useful because of convenience and the superior properties of the esters it produces, involves the reaction of the carboxylic acylating agents described above with one or more alcohols or phenols in ratios from about 0.5 equivalent to about 4 equivalents of
hydroxy compound per equivalent of acylating agent. The esterification is usually carried out at a temperature above about 100°C, or between 150°C and 300°C. The water formed as a by-product is removed by distillation as the esterification proceeds. The preparation of useful carboxylic ester dispersant is described in U.S. Patents 3,522,179 and 4,234,435, and their disclosures are incorporated by reference.

The carboxylic ester dispersants may be further reacted with at least one of the above described amines, including at least one of the above described polyamines. The amine is added in an amount sufficient to neutralize any nonesterified carboxyl groups. In one embodiment, the nitrogen-containing carboxylic ester dispersants are prepared by reacting about 1.0 to 2.0 equivalents, or about 1.0 to 1.8 equivalents of hydroxy compounds, and up to about 0.3 equivalent, or about 0.02 to about 0.25 equivalent of polyamine per equivalent of acylating agent.

In another embodiment, the carboxylic acid acylating agent may be reacted simultaneously with both the alcohol and the amine. There is generally at least about 0.01 equivalent of the alcohol and at least 0.01 equivalent of the amine although the total amount of equivalents of the combination should be at least about 0.5 equivalent per equivalent of acylating agent. These nitrogen-containing carboxylic ester dispersant compositions are known in the art, and the preparation of a number of these derivatives is described in, for example, U.S. Patents 3,957,854 and 4,234,435, which have been incorporated by reference previously.

In another embodiment, the dispersant may also be derived from a Mannich dispersant. Mannich dispersants are generally formed by the reaction of at least one aldehyde, at least one of the above described amine and at least one alkyl substituted hydroxyaromatic compound. The reaction may occur from room temperature to 225°C, or from 50°C to about 200°C, or from about 75°C to about 150°C, with the amounts of the reagents being such that the molar ratio of hydroxyaromatic compound to formaldehyde to amine is in the range from about (1:1:1) to about (1:3:3).
The first reagent is an alkyl substituted hydroxyaromatic compound. This term includes phenols (which are particularly useful), carbon-, oxygen-, sulfur- and nitrogen-bridged phenols and the like as well as phenols directly linked through covalent bonds (e.g. 4,4'bis(hydroxy)biphenyl), hydroxy compounds derived from fused-ring hydrocarbon (e.g., naphthols and the like); and polyhydroxy compounds such as catechol, resorcinol and hydroquinone. Mixtures of one or more hydroxyaromatic compounds can be used as the first reagent.

The hydroxyaromatic compounds are those substituted with at least one, and or not more than two, aliphatic or alicyclic groups having at least about 6 (usually at least about 30, or from at least 50) carbon atoms and up to about 400 carbon atoms, or up to about 300, or up to about 200. These groups may be derived from the above described polyalkenes. In one embodiment, the hydroxy aromatic compound is a phenol substituted with an aliphatic or alicyclic hydrocarbon-based group having an Mn of about 420 to about 10,000.

The second reagent is a hydrocarbon-based aldehyde, such as a lower aliphatic aldehyde. Suitable aldehydes include formaldehyde, benzaldehyde, acetaldehyde, the butyraldehydes, hydroxybutyraldehydes and heptanal, as well as aldehyde precursors which react as aldehydes under the conditions of the reaction such as paraformaldehyde, paraldehyde, formalin and methal. Formaldehyde and its precursors (e.g., paraformaldehyde, trioxane) are particularly useful. Mixtures of aldehydes may be used as the second reagent.

The third reagent is any amine described above. In one embodiment, the amine is a polyamine as described above. Mannich dispersants are described in the following patents: U.S. Patent 3,980,569; U.S. Patent 3,877,899; and U.S. Patent 4,454,059 (herein incorporated by reference for their disclosure to Mannich dispersants).

In one embodiment, the dispersant is a borated dispersant. The borated dispersant are prepared by reacting one or more of the above dispersant is a borating agent. Borating agents include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boric acid, tetraboric acid and metabolic acid, boron hydrides, boron amides and
various esters of boron acids. The boron esters include lower alkyl (1-7 carbon atoms) esters of boric acid. A particularly useful boron compound is boric acid.

The following example relate to borated dispersants.

Example D-1

A mixture of 372 grams (6 equivalents of boron) of boric acid and 3111 grams (6 equivalents of nitrogen) of an acylated nitrogen composition, obtained by reacting 1 equivalent of a polybutenyl (Mn=850) succinic anhydride, having an acid number of 113 (corresponding to an equivalent weight of 500), with 2 equivalents of a commercial ethylene amine mixture having an average composition corresponding to that of tetraethylenepentamine, is heated at 150 °C for 3 hours a then filtered. The filtrate is found to have a boron content of 1.64% and a nitrogen content of 2.56%.

Example D-2

(a) A reaction vessel is charged with 1000 parts of a polybutenyl (Mn=1000) substituted succinic anhydride, having a total acid number of 108, with a mixture of 275 grams of oil and 139 parts of a commercial mixture of polyamines corresponding to 85% E-100 amine bottoms and 15% diethylenetriamine. The reaction mixture is heated to 150 to 160 °C and the reaction temperature is maintained for four hours. The reaction is blown with nitrogen to remove water.

(b) A reaction vessel is charged with 1405 parts of the product of Example D-2a, 229 parts of boric acid, and 398 parts of diluent oil. The mixture is heated to 100 to 150 °C and the temperature maintained until water distillate ceases. The final product contains 2.3% nitrogen, 1.9% boron, 33% 100 neutral mineral oil and a total base number of 60.

Phosphorus Antiwear Agents

The lubricating compositions of the present invention may also include at least one phosphorus antiwear/extreme pressure agent. Generally the phosphorus antiwear/extreme pressure agent is present in an amount from about 0.01% to about 3%, or from about 0.1% to about 1.25%, or from about 0.2% to about 1% by weight.

Examples of phosphorus containing antiwear/extreme pressure agents include a metal thiophosphate; a phosphoric acid ester or salt thereof; a
phosphorus-containing carboxylic acid, ester, ether, or amide; and a phosphite. The phosphorus acids include the phosphoric, phosphonic, phosphinic and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric acid, thiophosphinic and thiophosphonic acids.

In one embodiment, the phosphorus containing antiwear/extreme pressure agent is a phosphorus acid ester prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from one, or about 3 carbon atoms. The alcohol generally contains up to about 30, or up to about 24, or up to about 12 carbon atoms. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorus acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide, and the like. Examples of phosphorus acids or anhydrides include phosphorus pentoxide, phosphorus pentasulfide and phosphorus trichloride. Lower phosphorus acid esters independently contain from 1 to about 7 carbon atoms in each ester group. The phosphorus acid ester may be a mono-, di- or triphosphoric acid ester. Alcohols used to prepare the phosphorus acid esters generally have from 1 to 30, or from about 2 to 24, or from about 4 to 18 carbon atoms. Examples include butyl, amyl, 2-ethylhexyl, hexyl, octyl, oleyl, and cresol alcohols. Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C_{18}-C_{28} primary alcohols having mostly C_{20} alcohols as determined by GLC (gas-liquid-chromatography)); and Alfol 22+ alcohols (C_{18}-C_{28} primary alcohols containing primarily C_{22} alcohols). Alfol alcohols are available from Continental Oil Company.

Another example of a commercially available alcohol mixtures are Adol 60 (about 75% by weight of a straight chain C_{22} primary alcohol, about 15% of a C_{20} primary alcohol and about 8% of C_{18} and C_{24} alcohols) and Adol 320 (oleyl alcohol). The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length from from about C_{6} to C_{18} are
available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C₁₀ alcohol, 66.0% of C₁₂ alcohol, 26.0% of C₁₄ alcohol and 6.5% of C₁₆ alcohol.

Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C₁₂ and C₁₃ alcohols; Neodol 25 is a mixture of C₁₂ and C₁₅ alcohols; and Neodol 45 is a mixture of C₁₄ to C₁₅ linear alcohols. Neodol 91 is a mixture of C₉, C₁₀ and C₁₁ alcohols.

Fatty vicinal diols also are useful and these include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha olefin fraction of C₁₁₋₁₄, and the latter is derived from a C₁₅₋₁₆ fraction.

Examples of useful phosphorus acid esters include the phosphoric acid esters prepared by reacting a phosphoric acid or anhydride with cresol alcohols. An example of these phosphorus acid esters is tricresylphosphate.

In another embodiment, the phosphorus antiwear/extreme pressure agent is a thiophosphorus acid ester or salt thereof. The thiophosphorus acid ester may be prepared by reacting a phosphorus sulfide, such as those described above, with an alcohol, such as those described above. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as thiophosphoric acids.

In one embodiment, the phosphorus acid ester is a monothio phosphoric acid ester or a monothiophosphate. Mono thiophosphates may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be elemental sulfur. The sulfur source may also be a monosulfide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. Elemental sulfur is a useful sulfur source. The preparation of monothiophosphates is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which are incorporated herein by reference for their disclosure of monothiophosphates, sulfur sources, and the process for making monothiophosphates. Mono thiophosphates may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition.
containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from about 30 C to about 100 C or higher) to form the monothiophosphate.

In another embodiment, the phosphorus antiwear/extreme pressure agent is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula (RO)₂PSSH wherein each R is independently a hydrocarbyl group containing from about 3 to about 30 carbon atoms. R generally contains up to about 18, or to about 12, or to about 8 carbon atoms. Examples R include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl, n-hexyl, methylisobutyl carbiny, heptyl, 2-ethylhexyl, isoctyl, nonyl, behenyl, decyl, dodecyl, and tridecyl groups. Illustrative lower alkylphenyl R groups include butylphenyl, amylphenyl, heptylphenyl, etc. Examples of mixtures of R groups include: 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl and isoctyl.

In one embodiment, the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene oxide is particularly useful. The glycols may be aliphatic glycols having from 1 to about 12, or about 2 to about 6, or 2 or 3 carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. patent 3,197,405 and U.S. patent 3,544,465 which are incorporated herein by reference for their disclosure to these.

The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

Example P-1

Phosphorus pentoxide (64 grams) is added at 58 C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl) phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-
phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C. The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and an acid number of 87 (bromophenol blue).

Example P-2

A mixture of 667 grams of phosphorus pentoxide and the reaction product of 3514 grams of diisopropyl phosphorodithioic acid with 986 grams of propylene oxide at 50°C is heated at 85°C for 3 hours and filtered. The filtrate contains 15.3% by weight phosphorus, 19.6% by weight sulfur, and an acid number of 126 (bromophenol blue).

Acidic phosphoric acid esters may be reacted with ammonia, an amine compound or a metallic base to form an ammonium or metal salt. The salts may be formed separately and then the salts of the phosphorus acid ester may be added to the lubricating composition. Alternately, the salts may also be formed in situ when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

The amine salts of the phosphorus acid esters may be formed from ammonia, or an amine, including the above described monoamines and polyamines. The metal salts of the phosphorus acid esters are prepared by the reaction of a metal base with the phosphorus acid ester. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, sulfates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. In one embodiment, the metal is magnesium, calcium, manganese or zinc. Examples of metal compounds which may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc.

In one embodiment, phosphorus containing antiwear/extreme pressure agent is a metal thiophosphate, or a metal dithiophosphate. The metal
thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl iso-octyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.

The following Examples P-3 to P-6 exemplify the preparation of useful phosphorus acid ester salts.

**Example P-3**

A reaction vessel is charged with 217 grams of the filtrate from Example P-1. A commercial aliphatic primary amine (66 grams), having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atom, is added over a period of 20 minutes at 25-60°C. The resulting product has a phosphorus content of 10.2% by weight, a nitrogen content of 1.5% by weight, and an acid number of 26.3.

**Example P-4**

Following the procedures of Examples P-1 and P-3, 1320 parts of the product described in P-1 was reacted with 584 parts of the amine of P-3. The final product has 8.4% phosphorus and 10% sulfur.

**Example P-5**

The filtrate of Example P-2 (1752 grams) is mixed at 25-82°C with 764 grams of the aliphatic primary amine used in of Example P-3. The resulting product has 9.9% phosphorus, 2.7% nitrogen, and 12.6% sulfur.

**Example P-6**

Phosphorus pentoxide (852 grams) is added to 2340 grams of iso-octyl alcohol over a period of 3 hours. The temperature increases from room temperature but is maintained below 65°C. After the addition is complete the reaction mixture is heated to 90°C and the temperature is maintained for 3 hours. Diatomaceous earth is added to the mixture, and the mixture is filtered. The filtrate has 12.4% phosphorus, a 192 acid neutralization number (bromophenol blue) and a 290 acid neutralization number (phenolphthalein).
The above filtrate is mixed with 200 grams of toluene, 130 grams of mineral oil, 1 gram of acetic acid, 10 grams of water and 45 grams of zinc oxide. The mixture is heated to 60-70°C under a pressure of 30 mm Hg. The resulting product mixture is filtered using a diatomaceous earth. The filtrate has 8.6% zinc and 7.0% phosphorus.

Example P-7

Alfol 8-10 (2628 parts, 18 moles) is heated to a temperature of about 45°C whereupon 852 parts (6 moles) of phosphorus pentoxide are added over a period of 45 minutes while maintaining the reaction temperature between about 45-65°C. The mixture is stirred an additional 0.5 hour at this temperature, and is there- after heated at 70 C for about 2-3 hours. Primene 81-R (2362 parts, 12.6 moles) is added dropwise to the reaction mixture while maintaining the temperature between about 30-50°C. When all of the amine has been added, the reaction mixture is filtered through a filter aid, and the filtrate is the desired amine salt containing 7.4% phosphorus (theory, 7.1%).

Example P-8

Phosphorus pentoxide (208 grams) is added to the product prepared by reacting 280 grams of propylene oxide with 1184 grams of O,O-di-isobutyl phosphorodithioic acid at 30-60°C. The addition is made at a temperature of 50-60°C and the resulting mixture is then heated to 80°C and held at that temperature for 2 hours. The commercial aliphatic primary amine identified in Example B-3 (384 grams) is added to the mixture, while the temperature is maintained in the range of 30-60°C. The reaction mixture is filtered through diatomaceous earth. The filtrate has 9.3% phosphorus, 11.4% sulfur, 2.5% nitrogen, and a base number of 6.9 (bromophenol blue indicator).

In another embodiment, the phosphorus antiwear/extreme pressure agent is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. Useful carboxylic acids are those having the formula RCOOH, wherein R is an aliphatic or alicyclic hydrocarbyl group preferably free from acetylenic unsaturation. R
generally contains from about 2, or from about 4 carbon atoms. R generally contains up to about 40, or up to about 24, or to up about 12 carbon atoms. In one embodiment, R contains from about 4, or from about 6 up to about 12, or up to about 8 carbon atoms. In one embodiments, R is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octadecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. A particularly useful carboxylic acid is 2-ethylhexanoic acid.

The metal salts may be prepared by merely blending a metal salt of a dithiophosphoric acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of dithiophosphoric acid to carboxylic acid is from about 0.5 up to about 400 to 1. The ratio may be from 0.5 up to about 200, or up to about 100, or up to about 50, or up to about 20 to 1. In one embodiment, the ratio is from 0.5 up to about 4.5 to one, or from about 2.5 up to about 4.25 to one. For this purpose, the equivalent weight of a dithiophosphoric acid is its molecular weight divided by the number of -PSSH groups therein, and the equivalent weight of a carboxylic acid is its molecular weight divided by the number of carboxyl groups therein.

A second method for preparing the metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio, such as those described above for the metal salts of the individual metal salts, and to react the acid mixture with one of the above described metal compounds. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus the metal salts may contain as many as 2 equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence. The temperature at which the metal salts are prepared is generally between about 30°C and about 150°C, or up to about 125°C. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for those disclosures.
In one embodiment, the phosphorus containing antiwear/extreme pressure agent is a phosphorus containing amide. The phosphorus containing amides are prepared by the reaction of one of the above described phosphorus acids, or a dithiophosphoric acid, with an unsaturated amide. Examples of unsaturated amides include acrylamide, N,N-methylene bis(acrylamide), methacrylamide, crotonamide, and the like. In one embodiment, the dithiocarbamate containing composition is derived from the reaction product of a diamylamine or dibutylamine with carbon disulfide which forms a dithiocarbamic acid or a salt which is ultimately reacted with a acrylamide. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374, which are incorporated by reference for their disclosures of phosphorus amides and their preparation.

In one embodiment, the phosphorus antiwear/extreme pressure agent is a phosphorus containing carboxylic ester. The phosphorus containing carboxylic esters are prepared by reaction of one of the above-described phosphorus acids, preferably a dithiophosphoric acid, and one of the unsaturated carboxylic acids or esters described herein. If the carboxylic acid is used, the ester may then be formed by subsequent reaction of the phosphoric acid-unsaturated carboxylic acid adduct with an alcohol, such as those described herein.

In one embodiment, the phosphorus containing antiwear/extreme pressure agent is a reaction product of a phosphorus acid, preferably a dithiophosphoric acid, and a vinyl ethers. The vinyl ether is represented by the formula \( R_1-\text{CH}=\text{CH-OR}_2 \) wherein \( R_1 \) is independently hydrogen or a hydrocarbyl group having from 1 up to about 30, or up to about 24, or up to about 12 carbon atoms. \( R_2 \) is a hydrocarbyl group defined the same as \( R_1 \). Examples of vinyl ethers include methyl vinyl ether, propyl vinyl ether, 2-ethylhexyl vinyl ether and the like.

In one embodiment, the phosphorus antiwear/extreme pressure agent is a phosphorus containing carboxylic ester contain at least one phosphite. The phosphite may be a di- or trihydrocarbyl phosphite. In one embodiment, each hydrocarbyl group independently contains from 1 to about 24 carbon atoms, or
from 1 to about 18 carbon atoms, or from about 2 to about 8 carbon atoms. Each hydrocarbyl group may be independently alkyl, alkenyl, or aryl. When the hydrocarbyl group is an aryl group, then it contains at least about 6 carbon atoms; or about 6 to about 18 carbon atoms. Examples of the alkyl or alkenyl groups include propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, etc.

Examples of aryl groups include phenyl, naphthyl, heptylphenol, etc. In one embodiment, each hydrocarbyl group is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl or phenyl, or butyl, oleyl or phenyl and or butyl or oleyl. One method of preparing phosphites includes reacting a lower (C₁₈) Phosphites and their preparation are known and many phosphites are available commercially.

Particularly useful phosphites are dibutyl hydrogen phosphite, dioleyl hydrogen phosphite, di(C₁₄H₉) hydrogen phosphite, and triphenyl phosphite.

Fatty Imidazoline or Fatty Acid-polyamine Reaction Product

The lubricating compositions also may include at least one fatty imidazoline or at least one reaction product of at least one fatty carboxylic acid and at least one polyamine. In one embodiment, the fatty imidazoline or reaction product of a fatty carboxylic acid of and at least one polyamine is present in an amount to provide from about 0.01% to about 0.7%, or from about 0.02% to about 0.4%, or from about 0.03% to about 0.2% by weight to the final lubricant.

The fatty imidazoline has fatty substituents containing from about 8 to about 30, or from about 12 to about 24 carbon atoms. The substituent may be saturated or unsaturated. Saturated substituents are particularly useful. In one aspect, the fatty imidazoline may be prepared by reacting a fatty carboxylic acid with a polyalkylenepolyamine, such as those discussed above.

The fatty carboxylic acids are generally mixtures of straight and branched chain fatty carboxylic acids containing about 8 to about 30 carbon atoms, or from about 12 to about 24, or from about 16 to about 18. Carboxylic acids include the polycarboxylic acids or carboxylic acids or anhydrides having from 2 to about 4 carbonyl groups, preferably 2. The polycarboxylic acids include succinic acids and anhydrides and Diels-Alder reaction products of unsaturated monocarboxylic acids with unsaturated carboxylic acids (such as acrylic, methacrylic, maleic, fumaric, crotonic and itaconic acids). In one embodiment, the fatty carboxylic acids are fatty monocarboxylic acids, having from about 8 to about 30, or from
about 12 to about 24 carbon atoms. Specific examples include such as octanoic, oleic, stearic, linoleic, dodecanoic, and tall oil acids. Stearic acid is particularly useful.

One or more fatty carboxylic acid is reacted with at least one polyamine. The polyamines may be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of the polyamines include alkylene polyamines and heterocyclic polyamines. Specific examples are described above.

A useful reaction product of a carboxylic acid and polyamine is made by reacting the above-described alkylene polyamines with a mixture of fatty acids having from 5 to about 30 mole percent straight chain acid and about 70 to 95 mole percent branch chain fatty acids. Among the commercially available mixtures are those known commonly in the trade as isostearic acid. These mixtures are produced as a by-product from the dimerization of unsaturated fatty acids as described in U.S. Patents 2,812,342; and 3,260,671. These patents are hereby incorporated by reference for their disclosure of these reaction products and methods of making the same.

The branched chain fatty acids can also include those in which the branch is not alkyl in nature, such as found in phenyl and cyclohexyl stearic acid and the chloro-stearic acids. Branched chain fatty carboxylic acid/alkylene polyamine products have been described extensively in the art. See, for example, U.S. Patents 3,110,673; 3,251,853; 3,326,801; 3,337,459; 3,405,064; 3,429,674; 3,468,639; and 3,857,791. These patents are hereby incorporated by reference for their disclosures of fatty acid/polyamine condensates for their use in lubricating oil formulations.

In another embodiment, the reaction product of a fatty carboxylic acid and a polyamine are further reacted with an epoxide. Epoxides are generally lower aliphatic epoxides, having from 1 to about 7 carbon atoms, or from 1 to about 5 carbon atoms, or from 2 to about 4 carbon atoms. Examples of these epoxides include ethylene oxide, propylene oxide, butylene oxide, cyclohexene oxide and octylene oxide. The epoxides generally react in an amount from about 0.5% to about 5% by weight of lower epoxide based on the total weight of the reaction product. The reaction generally occurs at a temperature above about 100 C. The reaction product of a fatty acid, polyamine and epoxide is described in U.S.
Patent 3,240,575 which is hereby incorporated by reference for its teachings to carboxylic acids, polyamines, epoxides and reaction products and methods of making the reaction products.

The following examples illustrate the reaction product of a fatty carboxylic acid of and at least one polyamine of the present invention.

EXAMPLE I-1

To 1133 parts of commercial diethylenetriamine heated at 110-150°C is slowly added 6820 parts of isostearic acid over a period of two hours. The mixture is held at 150°C for one hour and then heated to 180°C over an additional hour. Finally, the mixture is heated to 205°C over 0.5 hour; through this heating, the mixture is blown with nitrogen to remove volatiles. The mixture is held at 205-230°C for a total of 11.5 hours and then stripped at 230°C/20 torr to provide the desired acylated polyamine as a residue containing 6.2% nitrogen.

EXAMPLE I-2

To 205 parts of commercial tetraethylenepentamine heated to about 75°C there is added 1000 parts of isostearic acid while purging with nitrogen, and the temperature of the mixture is maintained at about 75E-110°C. The mixture then is heated to 220°C and held at this temperature until the acid number of the mixture is less than 10. After cooling to about 150°C, the mixture is filtered, and the filtrate is the desired acylated polyamine having a nitrogen content of about 5.9%.

EXAMPLE I-3

A mixture (565 parts by weight) of an alkylene amine mixture consisting of triethylenetetramine and diethylenetriamine in weight ratio of 3:1 is added at 20E-80°C to a mixture of equivalent amounts of a naphthenic acid having an acid number of 180 (1270 parts) and oleic acid (1110 parts; the total quantity of the two acids used is such as to provide one equivalent for each two equivalents of the amine mixture used). The reaction is exothermic. The mixture is blown with nitrogen while it is being heated to 240°C in 4.5 hours and thereafter heated at this temperature for 2 hours. Water is collected as the distillate. To the above residue ethylene oxide (140 parts) is added at 170E-180°C within a period of 2 hours while nitrogen is bubbled through the reaction mixture. The reaction
mixture is then blown with nitrogen for 15 minutes and diluted with 940 parts of xylene to a solution containing 25% of xylene. The resulting solution has a nitrogen content of 5.4% and a base number of 82 at pH of 4, the latter being indicative of free amino groups.

5 **Antifoam Agents**

In one embodiment, the lubricating compositions contain at least one antifoam agent. Antifoam agents are well-known in the art as silicone or fluorosilicone compositions. Such antifoam agents are available from Dow Corning Chemical Corporation and Union Carbide Corporation. Useful antifoam product is Dow FS-1265, Dow Corning DC-200, Union Carbide UC-L45 and polyacrylate antifoamer available from Monsanto Polymer Products Co. of Nitro, W. Va. known as PC-1244. Also, a siloxane polyether copolymer antifoamer available from OSI Specialties, Inc. of Farmington Hills, Mich. and may also be included. One such material is sold as SILWET-L-7220.

10 Polyacrylates or acrylic polymers are also known antifoam agents are disclosed in U.S. Patent 3,166,508 and UK patent publication GB 2,234,978. These references are hereby incorporated by reference. Polyacrylates are commercially available from several manufactures and the types used as antifoamants are typically polymers and copolymers comprising one or more of ethyl acrylate and 2-ethylhexyl acrylate, along with other monomers, such as vinylacetate, as is known to those skilled in the art. A useful antifoam agent is a copolymer of ethyl acrylate and 2-ethylhexyl acrylate sold by Monsanto as PC-1244 defoamer was used as the polyacrylate. The antifoam agents are included in the compositions of this invention at a level from about 100 to 2000, or from about 150 to 1500, or from about 200 to 1000 parts per million with the active ingredient being on an oil-free basis.

15 **Antioxidant**

In another embodiment, the lubricant may also contain one or more antioxidants. In one embodiment, the antioxidant is present in an amount from about 0.001% to about 5%, or from about 0.01% to about 2%, or from about 0.05% to about 1% by weight of the lubricating composition. The antioxidants may be present in a total amount generally from about 1.5% up to about 10%, or about 1.8% up to about 8%, or from about 1.9% up to about 6% by weight.
another embodiment, the lubricating composition contains at least about 1% by weight of an amine antioxidant, a dithiocarbamate antioxidant, or mixture thereof. In one embodiment, the antioxidant is an amine antioxidant, or a dithiocarbamate antioxidant. In one embodiment, the antioxidants are ashless, i.e., free of metal.

In another embodiment, the antioxidant is other than a polyphenol.

Amine antioxidants include alkylated aromatic amines and heterocyclic amines. The alkylated aromatic amines include compounds represented by the formula \( \text{Ar}^1-\text{NR}_1-\text{Ar}^2 \), wherein \( \text{Ar}^1 \) and \( \text{Ar}^2 \) are independently mononuclear or polynuclear, substituted or unsubstituted aromatic groups; and \( \text{R}_1 \) is hydrogen, halogen, OH, NH\(_2\), SH, NO\(_2\) or a hydrocarbyl group having from 1 to about 50 carbon atoms. The aromatic group as represented by "Ar", as well as elsewhere in other formulae in this specification and in the appended claims, may be mononuclear or polynuclear. Examples of mononuclear Ar moieties include benzene moieties, such as 1,2,4-benzenetriyl; 1,2,3-benzenetriyl; 3-methyl-1,2,4-benzenetriyl; 2-methyl-5-ethyl-1,3,4-benzenetriyl; 3-propoxy-1,2,4,5-benzenetetrayl; 3-chloro-1,2,4-benzenetriyl; 1,2,3,5-benzenetetrayl; 3-cyclohexyl-1,2,4-benzenetriyl; and 3-azocyclopentyl-1,2,5-benzenetriyl, and pyridine moieties, such as 3,4,5-azabenzene; and 6-methyl-3,4,5-azabenzene. The polynuclear groups may be those where an aromatic nucleus is fused at two points to another aromatic nucleus, such as naphthyl and anthracenyl groups.

Specific examples of fused ring aromatic moieties Ar include: 1,4,8-naphthylene; 1,5,8-naphthylene; 3,6-dimethyl-4,5,8(1-azonaphthalene); 7-methyl-9-methoxy-1,2,5, 9-anthracenetetrayl; 3,10-phenanthrylene; and 9-methoxy-benz(a)phenanthrene-5,6,8,12-yl. The polynuclear group may be those where at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages. These bridging linkages may be chosen from the group consisting of alkylene linkages, ether linkages, keto linkages, sulfide linkages, and polysulfide linkages of 2 to about 6 sulfur atoms. Specific examples of Ar when it is linked polynuclear aromatic moiety include: 3,3,4,4',5-bibenzenetetrayl; di(3,4-phenylene)ether; 2,3-phenylene-2,6-naphthenemethane; and 3-methyl,9H-fluorene-1,2,4,5,8-yl; 2,2-di(3,4-phenylene)propane; sulfur-coupled 3-methyl-1,2,4-benzatriyl (having 1 to about 10 thiomethylphenylene groups); and aminocoupled 3-methyl-1,2,4-benzatriyl (having 1 to about 10 aminomethylphenylene
groups). Typically Ar is a benzene nucleus, lower alkylene bridged benzene nucleus, or a naphthalene nucleus.

In another embodiment, the alkylated aromatic amine is represented by the formula R₂-Ar-NH-Ar-R₃, wherein R₂ and R₃ are independently hydrogen or hydrocarbyl groups having from 1 to about 50, or from about 4 to about 20 carbon atoms. Examples of aromatic amines include p,p'-dioctyl diphenylamine; octylphenyl-beta-naphthylamine; octylphenyl-"-naphthylamine, phenyl-"-naphthylamine; phenyl-beta-naphthylamine; p-octylphenyl-"-naphthylamine and 4-octylphenyl-1-octyl-beta-naphthylamine and di(nonylphenyl)amine, with di(nonylphenyl)amine preferred. U.S. Patents 2,558,285; 3,601,632; 3,368,975; and 3,505,225 disclose diarylamines useful as antioxidants. These patents are incorporated herein by reference.

In another embodiment, the antioxidant may be a phenothiazine. Phenothiazines include phenothiazine, substituted phenothiazine, or derivatives so as those described in U.S. Patents 4,785,095, and 5,883,057 and the disclosures of the patent are hereby incorporated by reference for its teachings of such methods and compounds. In one embodiment, a dialkyl diphenylamine is treated with sulfur at an elevated temperature such as in the range of 145°C to 205°C for a sufficient time to complete the reaction. A catalyst, such as iodine, may be utilized to establish the sulfur bridge.

Phenothiazine and its various derivatives may be converted to the above compounds by contacting the phenothiazine compound containing the free NH group with a thioalcohol of the formula R₅SR₆OH where R₆ is an alkylene, alkenylene or an aralkylene group, or mixtures thereof, R₅ is selected from the group consisting of higher alkyl groups, or an arkenyl, aryl, alkaryl or aralkyl group and mixtures thereof; each R₆ is independently alkyl, arkenyl, aryl, alkyl, aryalkyl, halogen, hydroxyl, alkoxy, alkylthio, arylthio, or fused aromatic rings, or mixtures thereof; a and b are each independently 0 or greater. In one embodiment, R₆ contains from about 2 to about 8, or two or three carbon atoms. R₅ typically contains from about 3 to about 30, or from about 4 to about 15 carbon atoms. R₆ contains from 1 to about 50, or from about 4 to about 30, or from 6 to about 20 carbon atoms. The thioalcohol may be obtained by the
reaction of a mercaptan (e.g. a C_{4-30} mercaptan), such as hexanethiol, octanethiol and dodecanethiol, with an alkyne oxide, such as ethylene or propylene oxide under basic conditions. Alternatively, the thioalcohol may be obtained by reacting a terminal olefin, such as those described herein, with mercaptoethanol under free radical conditions. In another embodiment, the phonothiazone derivatives are prepared by the reaction with the thioalcohols described above are oxidized with an oxidizing agent, such as hydrogen peroxide, in a solvent such as glacial acetic acid or ethanol under an inert gas blanket. The partial oxidation takes place conveniently at from about 20°C to about 150°C.

In another embodiment, the antioxidant (A) is at least one phenol antioxidant. The phenol antioxidants include metal and metal free hindered phenols. Alkylene coupled derivatives of hindered phenols and phenol sulfides or sulfur coupled phenols may also be used. Hindered phenols are defined as those containing a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds wherein the hydroxyl groups are in the o- or p-position to each other. The phenols may have one or more alkyl groups. In one embodiment, alkyl groups are derived from one or more of the above polyalkenes. The alkyl groups may be derived from polymers of ethylene, propylene, 1-butene and isobutene, propylene tetramers or trimers are particularly useful. Examples of R_{2} groups include hexyl, heptyl, octyl, decyl, dodecyl, tripropenyl, tetrapropenyl, etc. Examples of R_{1}, R_{2} and R_{3} groups include propyl, isopropyl, butyl, sec-butyl, tert-butyl, heptyl, octyl, and nonyl. In another embodiment, each R_{1} and R_{3} are tertiary groups, such as tert-butyl or tert-amyl groups. The phenolic compounds may be prepared by various techniques, and in one embodiment, such phenols are prepared in stepwise manner by first preparing the para-substituted alkylphenol, and thereafter alkylating the para-substituted phenol in the 2- and/or 6-position as desired. When it is desired to prepare coupled phenols, the second step alkylation is conducted under conditions which result in the alkylation of only one of the positions ortho to the hydroxyl group. Examples of useful phenolic materials include: 2-t-butyl-4-heptylphenol; 2-t-butyl-4-octylphenol; 2-t-butyl-4-
dodecylphenol; 2,6-di-t-butyl-4-butyphenol; 2,6-di-t-butyl-4-heptylphenol; 2,6-di-
t-butyl-4-dodecylphenol; 2,6-di-t-butyl-tetrapropenylphenol; 2-methyl-6-di-t-butyl-
4-heptylphenol; 2,6-di-t-butyl-tripropenylphenol; 2,4-dimethyl-6-t-butylphenol;
2,6-t-butyl-4-ethylphenol; 4-t-butyl catechol; 2,4-di-t-butyl-p-cresol; 2,6-di-t-butyl-
4-methylphenol; and 2-methyl-6-di-t-butyl-4-dodecylphenol. Examples of the
ortho coupled phenols include: 2,2'-bis(6-t-butyl-4-heptylphenol); 2,2'-bis(6-t-
butyl-4-octylphenol); 2,6-bis-(1'-methylcyclohexyl)-4-methylphenol; and 2,2'-
bis(6-t-butyl-4-dodecylphenol).

Alkylene-coupled phenolic compounds may be prepared from the phenols
by reaction of the phenolic compound with an aldehyde, typically those
containing from one to about eight carbon atoms, such as formaldehyde or
acetaldehyde, aldehyde precursors, such as paraformaldehyde or trioxane, or a
ketone, such as acetone. The alkylene-coupled phenols may be obtained by
reacting from 0.3 to about 2 moles a phenol with 1 equivalent of an aldehyde or
ketone. Procedures for coupling of phenolic compounds with aldehydes and
ketones are known to those in the art. Examples of phenolic compounds include
2,2'-methylenebis(6-t-butyl-4-heptylphenol); 2,2'-methylenebis(6-t-butyl-4-octylphenol); 2,2'-methylenebis(4-dodecyl-6-t-butylphenol); 2,2'-methylenebis(4-
ctyl-6-t-butylphenol); 2,2'-methylenebis(4-octylphenol); 2,2'-methylenebis(4-
dodecylphenol); 2,2'-methylenebis(4-heptylphenol); 2,2'-methylenebis(6-t-butyl-
4-dodecylphenol); 2,2'-methylenebis(6-t-butyl-4-tetrapropenylphenol); and 2,2'-
methylenebis(6-t-butyl-4-butyl phenol).

In another embodiment, the antioxidant is a metal-free (or ashless)
alkyphenol sulfide or sulfur coupled phenols. The alkylphenols from which the
sulfides are prepared also may comprise phenols of the type discussed above
and represented by Formula III wherein R₃ is hydrogen. For example, the
alkylphenols which can be converted to alkylphenol sulfides include: 2-t-butyl-4-
heptylphenol; 2-t-butyl-4-octylphenol; and 2-t-
butyl-4-dodecylphenol; 2-t-butyl-4-tetrapropenylphenol. The term "alkyphenol sulfides" is meant to include di-
(alkyphenol) monosulfides, disulfides, and polysulfides, as well as other
products obtained by the reaction of the alkylphenol with sulfur monochloride,
sulfur dichloride or elemental sulfur. One mole of phenol typically is reacted with
about 0.5-1.5 moles, or higher, of sulfur compound. For example, the
alkylphenol sulfides are readily obtained by mixing, one mole of an alkylphenol and 0.5-2.0 moles of sulfur dichloride. The reaction mixture is usually maintained at about 100°C for about 2-5 hours, after which time the resulting sulfide is dried and filtered. When elemental sulfur is used, temperatures from about 150-250°C or higher are typically used. It is also desirable that the drying operation be conducted under nitrogen or a similar inert gas. A particularly useful alkylphenol sulfide is thio-bis(tetrapropenylphenate).

Suitable basic alkylphenol sulfides are disclosed, for example, in U.S. Patents 3,372,116; 3,410,798; and 4,021,419, which are hereby incorporated by reference. These sulfur-containing phenolic compositions described in U.S. Patent 4,021,419 are obtained by sulfurizing a substituted phenol with sulfur or a sulfur halide and thereafter reacting the sulfurized phenol with formaldehyde or an aldehyde precursor, e.g., paraformaldehyde or trioxane. Alternatively the substituted phenol may be first reacted with formaldehyde or paraformaldehyde and thereafter reacted with sulfur or a sulfur halide to produce the desired alkylphenol sulfide.

Oil of Lubricating Viscosity

The lubricant and concentrate include an oil of lubricating viscosity. The oil of lubricating viscosity is generally present in a major amount (i.e. an amount greater than about 50% by weight). In one embodiment, the oil of lubricating viscosity is present in an amount greater than about 60%, or greater than about 70%, or greater than about 80% by weight of the composition. The oils of lubricating viscosity include natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalpha-olefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Unrefined, refined, and rerefined oils, either natural or synthetic, may be used in the compositions of the present invention. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3,
line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

In one embodiment, the oil of lubricating viscosity is a polyalpha-olefin (PAO). Typically, the polyalpha-olefins are derived from monomers having from about 3 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 decene. These PAOs may have a viscosity from about 3 to about 150, or from about 4 to about 100, or from about 4 to about 8 cSt at 100°C. Examples of PAOs include 4 cSt polyolefins, 6 cSt polyolefins, 40 cSt polyolefins and 100 cSt polyalphaolefins.

In one embodiment, the oil of lubricating viscosity are selected to provide lubricating compositions with a kinematic viscosity of at least about 3.5 cSt, or at least about 4.0 cSt at 100°C. In one embodiment, the lubricating compositions have an SAE gear viscosity grade of at least about SAE 75W. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-140, 80W-90, 80W-140, 85W-90, or 85W-140.

In one embodiment, the oil of lubricating viscosity is a mineral oil. The mineral oils have an iodine number of less than 9 and/or at least about 45% of the saturates present as aliphatic saturates. Iodine value is determined according to ASTM D-460. In one embodiment, the mineral oil has a iodine value less than about 8, or less than about 6, or less than about 4. The saturates level are determined by mass spectrometer. By mass spectroscopy, Group I stocks have about 70% saturates, Group II stocks have about 95% to about 98% saturates and Group III stocks have about 98%-100% saturates. Group II stocks have greater than 50% of their saturates present as cyclopentane compounds. The saturates of the mineral oils used in the present invention typically have at least about 45%, or at least about 50%, or at least about 60% aliphatic saturates. These aliphatic saturates are often referred to as paraffinic saturates. The cyclic saturates are generally referred to as cyclopentane saturates. Cyclic saturates compose the balance of the saturates in the mineral oils. The inventors have discovered that mineral oils having a
higher proportion of aliphatic saturates have better oxidation properties and low temperature properties.

As use herein the term "minerel oil" refers to oils of lubricating viscosity which are derived from petroleum crude. The petroleum crudes may be subjected to processing such as hydprocracking, hydrocracking, and isomerizing. Hydroprocessing includes processes such as sequential isocracking, isodewaxing and hydrofinishing. These mineral oils are those referred to as Group III basestock or base oils. In one embodiment, the mineral oil has less than 0.3% or less than 0.1% sulfur. In another embodiment, the oils of lubricating viscosity generally have a viscosity index of 120 or more.

Examples of useful oils of lubricating viscosity include HVI and XHVI basestocks, such isomerized wax base oils and UCBO (Unconventional Base Oils) base oils. Specific examples of these base oils include 100N isomerized wax basestock (0.01% sulfur/ 141 VI), 120N isomerized wax basestock (0.01% sulfur/149 VI), 170N isomerized wax basestock (0.01% sulfur/142 VI), and 250N isomerized wax basestock (0.01% sulfur/146 VI); refined basestocks, such as 250N solvent refined paraffinic mineral oil (0.16% sulfur/89 VI), 200N solvent refined naphthenic mineral oil (0.2% sulfur/60 VI), 100N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/98 VI), 240N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/98 VI), 80N solvent refined/ hydrotreated paraffinic mineral oil (0.08% sulfur/127 VI), and 150N solvent refined/ hydrotreated paraffinic mineral oil (0.17% sulfur/127 VI). Further examples of the mineral oils include those Group III basestocks made by Texaco such as the TEXHVI stocks which include TEXHVI-100N (95% saturates, 125 viscosity index and 0.02% sulfur); TEXHVI-70N (97.8% saturates, 123 viscosity index and 0.02% sulfur); Texaco "MOTIVA" TEXHVI 90N-100N (100% saturates, 125 viscosity index and 0.01% sulfur); and "MOTIVA" TEXHVI 75N (100% saturates, 125 viscosity index and 0.0% sulfur). Examples of useful Group III basestocks made by Chevron include UCBO 200N (100% saturates, 142 viscosity index and 0.005% sulfur); UCBO 100N (100% saturates, 129 viscosity index, and 0.004% sulfur).
Polymers

In one embodiment, the multigrade lubricant will have at least one polymer present. The polymer generally is present in an amount from about 3% to about 40%, or from about 5% to about 35%, or from about 10% to about 30% by weight of the lubricating composition. The polymers include a polyalkene or derivative thereof, an ethylene-"-olefin copolymer, an ethylene-propylene polymer, an "-olefin-unsaturated carboxylic reagent copolymer, a polyacrylate, a polymethacrylate, a hydrogenated interpolymer of an alkenylarene and a conjugated diene, and mixtures thereof. Here, and elsewhere in the specification and claims, any member of a genus (or list) may be excluded from claims.

In one embodiment, the polymer is characterized by an Mw (weight average molecular weight) of less than about 50,000, or less than about 45,000, or less than about 40,000. In one embodiment, the polymer has an Mw of less than about 25,000, or less than about 10,000, or less than about 7,000. Typically the polymer has an Mw of at least about 1,000, or at least about 2,000, or at least about 3,000. In one embodiment, the polymer is characterized by an Mn (number average molecular weight) of up to about 6000, or up to about 5000. Generally, the polymer is characterized by having an Mn from about 800 to about 6000, or from about 900 to about 5000, or from about 1000 to 4000. In another embodiment, the polymers have a Mn from about 1300 to about 5000, or from about 1500 to about 4500, or from about 1700 to about 3000. The polymers also generally have a Mw/Mn from about 1.5 to about 8, or from about 1.8 to about 6.5, or from about 2 to about 5.5.

In one embodiment, the polymer may be a sheared polymer of higher molecular weight, e.g. greater than 50,000. In this embodiment, a higher molecular weight polymer is sheared to the desired molecular weight. The shearing may be done in any suitable apparatus, such as an extruder, an injector, an FZG apparatus, etc.

The abbreviation Mw and Mn is the conventional symbol representing weight average and number average molecular weight, respectively. Gel permeation chromatography (GPC) is a method which provides both molecular weights as well as the entire molecular weight distribution of the polymers. For
purpose of this invention a series of fractionated polymers of isobutene, 
polyisobutene, is used as the calibration standard in the GPC. The techniques 
for determining n and w values of polymers are well known and are described in 
numerous books and articles. For example, methods for the determination of n 
and molecular weight distribution of polymers is described in W.W. Yan, J.J. 
Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs," J. Wiley 

In one embodiment, the polymer is one of the polyalkenes described 
herein. In another embodiment, the polymer is a derivative of a polyalkene.

The derivatives are typically prepared by reacting one or more of the above 
polyalkenes or a halogenated derivative thereof with an unsaturated reagent. 
The halogenated polyalkenes are prepared by reacting a polyalkene with a 
halogen gas, such as chlorine. The preparation of these materials is known to 
those in the art. The unsaturated reagents include unsaturated amines, ethers, 
and unsaturated carboxylic reagents, such as unsaturated acids, esters, and 
anhydrides. Examples of unsaturated amines include unsaturated amides, 
unsaturated imides, and nitrogen containing acrylate and methacrylate esters. 
Specific examples of unsaturated amines include acrylamide, N,N,N-methylene 
bis(acrylamide), methacrylamide, crotonamide, N-(3,6-diazaheptyl) maleimide, 
N-(3-dimethylaminopropyl) maleimide, N-(2-methoxyethoxyethyl) maleimide, N-
vinyl pyrrolidinone, 2- or 4-vinyl pyridine, dimethylaminoethyl methacrylate and 
the like.

In one embodiment, the unsaturated carboxylic reagent is an acid, 
anhydride, ester, or mixtures thereof. If an ester is desired, it can be prepared 
by reacting an unsaturated carboxylic acid or anhydride with a polyalkene or 
halogenated derivative thereof and subsequently reacting the reaction product 
with an alcohol to form the ester. The unsaturated carboxylic reagents include 
acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 2-phenylpropenoic 
acid, maleic acid, maleic anhydride, fumaric acid, mesaconic acid, itaconic acid 
and citraconic acid maleic, fumaric, acrylic, methacrylic, itaconic, and citraconic 
acids, esters, and anhydrides (where possible). The esters may be represented 
by one of the formulae: (R₁)₂C=C(R₁)C(O)OR₂, or R₂O-(O)C-HC=CH-C(O)OR₂, 
wherein each R₁ and R₂ are independently hydrogen or a hydrocarbyl group.
having 1 to about 30, or to about 12, or to about 8 carbon atoms, \( R_1 \) is hydrogen or an alkyl group having from 1 to about 6 carbon atoms. In one embodiment, \( R_1 \) is preferably hydrogen or a methyl group. In another embodiment, \( R_2 \) is an alkyl or hydroxyalkyl group having from about 1 to about 30, or from 2 to about 24, or from about 3 to about 18 carbon atoms. \( R_2 \) may be derived from one or more alcohols described below. Unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-2-hydroxypropyl acrylate, ethyl maleate, butyl maleate and 2-ethylhexyl maleate.

The above list includes mono- as well as diesters of maleic, fumaric, and itaconic acids and anhydrides.

The polyalkene derivatives are prepared by means known to those in the art. These materials have been referred to as hydrocarbyl substituted carboxylic acylating agents, and are discussed below. U. S. Patents 3,219,666 and 4,234,435 describe the polyalkene derivatives and methods of making the same and are incorporated for such descriptions.

In another embodiment, the polymer is an ethylene-"-olefin copolymer. Typically, the copolymer is a random copolymer. The copolymer generally has from about 30% to about 80%, or from about 50% to about 75% by mole of ethylene. The "-olefins include butene, pentene, hexene or one more of the described above described "-olefins. In one embodiment, the "-olefin contains from about 3 to about 20, or from about 4 to about 12 carbon atoms. In one embodiment, the ethylene-"-olefin copolymers have an Mw from about 10,000 up to about 40,000, or from about 15,000 up to about 35,000, or from about 20,000 up to about 30,000. In another embodiment, the ethylene-"-olefin copolymers have an n from about 800 to about 6000, or from about 1500 to about 5000, or from about 2000 to about 4500. Examples of ethylene-"-olefins copolymers include ethylene-butene copolymers and ethylene-octene copolymers. Examples of commercially available copolymers include Lucant HC 600 and Lucant HC 2000 (Mw=25,000), available from Mitsui Petrochemical Co., Ltd.

In another embodiment, the polymer is an ethylene propylene polymer. These polymers include ethylene propylene copolymers and ethylene propylene terpolymers. When the ethylene propylene polymer is an ethylene propylene
copolymer (EPM, also called EPR polymers), it may be formed by
copolymerization of ethylene and propylene under known conditions, such as
Ziegler-Natta reaction conditions. In one embodiment, ethylene propylene
copolymers contain units derived from ethylene in an amount from about 40% to
about 70%, or from about 50% to about 60%, or about 55% by mole, the
remainder being derived from propylene. The molecular weight distribution may
be characterized by a polydispersity (Mw/Mn) from about 1 to about 8, or from
about 1.2 to about 4.

In another embodiment, the ethylene propylene polymer is a terpolymer of
ethylene, propylene and a diene monomer. In one embodiment, the diene is a
conjugated diene. The dienes are disclosed herein. The terpolymers are
produced under similar conditions as those of the ethylene propylene
copolymers. Useful terpolymers contain units derived from ethylene in amount
from about 10% to about 80%, or from about 25% to about 85%, or about 35% to
about 60% by mole, and units derived from propylene in amount from about 15%
to about 70%, or from about 30% to about 60% by mole, and units derived from
diene third monomer in amount from about 0.5% to about 20%, or from about
1% to about 10%, or about 2% to about 8% by mole. The following table
contains examples of ethylene propylene terpolymers.

<table>
<thead>
<tr>
<th>Example</th>
<th>Ethylene</th>
<th>Propylene</th>
<th>Diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42%*</td>
<td>53%</td>
<td>5% 1,5 heptadiene</td>
</tr>
<tr>
<td>B</td>
<td>48%</td>
<td>48%</td>
<td>4% dicyclopentadiene</td>
</tr>
<tr>
<td>C</td>
<td>45%</td>
<td>45%</td>
<td>10% 5-ethylidene-2-norbornene</td>
</tr>
<tr>
<td>D</td>
<td>48%</td>
<td>48%</td>
<td>4% 1,6 octadiene</td>
</tr>
<tr>
<td>E</td>
<td>48%</td>
<td>48%</td>
<td>4%, 4 cyclohexadiene</td>
</tr>
<tr>
<td>F</td>
<td>50%</td>
<td>45%</td>
<td>4% 5-methylene-2-norbornene</td>
</tr>
</tbody>
</table>

*Percentages are by mole

In one embodiment, the ethylene propylene polymer is a terpolymer of
ethylene, propylene and dicyclopentadiene or ethylidene norbornene, available
commercially as Trilene elastomers from the Uniroyal Corporation. A useful
ethylene propylene terpolymer is Trilene CP-40. The ethylene propylene
polymers are prepared by means known to those in the art. U.S. Patent 3,691,078 describes ethylene propylene polymers and methods of preparing them, and is incorporated by reference for such disclosures.

In another embodiment, the polymer is a copolymer of an "-olefin and an unsaturated reagent. The "-olefins may be any of those discussed above, and include propylene, 1-butene, 2-methyl propene, 2-methyl-1-octene, and 1-decene. The unsaturated reagents are described above. The unsaturated carboxylic reagents include acrylates, methacrylates, maleates and fumarates. The "-olefin-unsaturated carboxylic reagent polymers are prepared by means known to those in the art. Examples of "-olefin-unsaturated carboxylic reagent copolymers include poly(octene-co-ethylacrylate), poly(decene-co-butylmethacrylate), poly(hexene-co-maleic anhydride), poly(octene-co-methyl fumarate) and the like.

In another embodiment, the polymer is a polyacrylate or polymethacrylate. The polyacrylates and polymethacrylates include homopolymers and interpolymers of one or more of the above described acrylic or methacrylic acids or esters. The polyacrylates and polymethacrylates include the Acryloid 1019 polymers, available from Rohm and Haas Company, Garbacryl 6335 available from Societe Francaise d’Organo-Synthese (SFOS), LZ 7720C available from The Lubrizol Corporation, and Viscoplex 0-101 polymers, available from Rohm Darmstadt.

In another embodiment, the polymer is a hydrogenated interpolymer of an vinyl substituted aromatic compound and a conjugated diene. The interpolymers include diblock, triblock and random block interpolymers. The vinyl substituted aromatic compounds generally have from about 8 to about 20, or from about 8 to about 18, or from about 8 to about 12 carbon atoms. Examples of vinyl substituted aromatics include styrene, "-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-t-butylstyrene, with styrene being preferred. The conjugated dienes are described above. Isoprene and 1,3-butadiene are preferred conjugated dienes.

The vinyl substituted aromatic content of these copolymers is in the range from about 20% to about 70%, or from about 40% to about 60% by weight. Thus, the conjugated diene content is in the range from about 30% to about
80%, or from about 40% to about 60% by weight. These interpolymers are prepared by conventional methods well known in the art. Such copolymers usually are prepared by anionic polymerization using, for example, an alkali metal hydrocarbon (e.g., sec-butylthiium) as a polymerization catalyst.

Examples of suitable hydrogenated copolymers of a vinyl substituted aromatic compound and a conjugated diene include Shellvis-40, and Shellvis-50, both hydrogenated styrene-isoprene block copolymers, manufactured by Shell Chemicals.

**Fluidizing Agent**

The lubricating compositions may additionally contain at least one fluidizing agent. Generally, the fluidizing agent is present in an amount up to about 30% by weight. Typically the fluidizing agent is present in an amount from about 3% to about 30%, or from about 5% to about 28%, from about 10% to about 27%, or from about 15% to about 25% by weight of the lubricating composition. The amount of fluidizing agent equals the total amount of fluidizing agents in the lubricating compositions.

In one embodiment, the fluidizing agent is at least one member selected from the group consisting of an alkylated aromatic hydrocarbon, a naphthenic oil, a poly"-olefin having a kinematic viscosity from about 3 to about 20 cSt at 100°C, a carboxylic acid esters, and mixtures of two or more thereof. The alkylated aromatic hydrocarbons typically include mono- or di- (or mono-) substituted benzenes wherein the substituents are hydrocarbon-based groups having from about 8 to about 30, or from about 10 to about 14 carbon atoms. An example is Alkylate A-215 (a 237 molecular weight alkylated benzene) and Alkylate A-230 (a 230 molecular weight alkylated benzene) available from Monsanto.

The naphthenic oils are those derived from naphthenic crudes such as found in the Louisiana area. The viscosity of such naphthenic oils at 40°C generally is less than 4 centistokes and more generally within the range of from about 3.0 to about 3.8 centistokes. At 100°C the viscosity of the desirable naphthenic crudes is within the range of about 0.8 to about 1.6 centistokes.

The poly"-olefins (PAOs) are described above. Examples of useful PAOs include those derived from one or more of the above olefins, such as the"-
olefins. These PAOs may have a viscosity from about 2 to about 30, or from about 3 to about 20, or from about 3 to about 8 cSt at 100°EC. Examples of PAOs include 4 cSt poly"-olefins, 6 cSt poly"-olefins, and 8 cSt poly"-olefins. A particularly useful PAO is derived from decene.

The carboxylic ester fluidizing agents are reaction products of dicarboxylic esters with alcohols having from about 1 to about 30, or from about 2 to about 18, or from about 3 to about 12 carbon atoms. The alcohols are described below and include methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, decyl and dodecyl alcohols. The dicarboxylic acids generally contain from about 4 to about 18, or from about 4 to about 12, or from about 4 to about 8 carbon atoms. Examples of dicarboxylic acids include phthalic acid, succinic acid, alkyl (C₁₋₂₄ )succinic acids, azelaic acid, adipic acid, and malonic acid. Particularly useful esters are dicarboxylic esters of C₁₋₁₂ alcohols, such as esters of propyl, butyl, pentyl, hexyl, and octyl alcohols and azelaic acid. In one embodiment, the lubricating compositions contain less than about 20%, or less than about 15% by weight of carboxylic ester fluidizing agent.

The above-described mineral oil may be used with commercially available gear and transmission concentrates such as those sold by Exxon, Lubrizol, Ethyl and Mobil corporations. In this embodiment, those commercial concentrates are diluted with the basestocks to form the transmission and gear formulations.

The combinations may be used in lubricants or in concentrates. The concentrate may contain the above combinations and/or other components used in preparing fully formulated lubricants. The concentrate also contains a substantially inert organic diluent, which includes kerosene, mineral distillates, or one or more of the oils of lubricating viscosity discussed herein. The combinations are present in a final product, blend, or concentrate in any amount effective to act as an antiwear, antiweld, and/or extreme pressure agents in lubricating compositions.

In one embodiment, the lubricating composition is free of sulfurized olefins and fatty acids or esters. In another embodiment, the lubricating composition is free of overbased metal. In another embodiment, the lubricating composition is free of zinc dithiophosphates. In another embodiment, the lubricating
composition is free of added lead compounds, such as lead napthanates, dithiophosphates and dithiocarbamates. In another embodiment, the lubricating composition is free of succinimides derived from olefins or polyolefins and ammonia or a mono-amine. In another embodiment, the lubricating composition is free of detergents or overbased metal salts of acidic organic compounds.

Other Additives

The invention also contemplates the use of other additives together with the above combinations. Such additives include, for example, detergents and dispersants, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, antiwear agents, color stabilizers and anti-foam agents.

The detergents are exemplified by oil-soluble neutral and basic salts (i.e. overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids, such as those described above.

The oil-soluble neutral or basic salts of alkali or alkaline earth metal salts may also be reacted with a boron compound. Examples of useful overbased and borated overbased metal salts include sodium, calcium and magnesium overbased and borated overbased sulfonates and carboxylates, including the above hydrocarbtyl substituted carboxylic acylating agents.

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated waxes; sulfurized alkylphenols; phosphosulfurized hydrocarbons, such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; metal thiocarbamates, such as zinc diocetylthiocarbamate, and barium diheptylphenyl dithio carbamate; and ashless dithiocarbamates such as reaction products of a dithiocarbamic acid and an unsaturated acid, ester, anhydride, amide, ether, or imide. Many of the above-mentioned extreme pressure agents and corrosion- and oxidation-inhibitors also serve as antiwear agents.

Pour point depressants are an additive often included in the lubricating oils described herein. Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers.
Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715, which are hereby incorporated by reference for their relevant disclosures.

It is understood that any of the above described additives that are taught as potential ingredients may be restricted from the lubricating compositions.

The following examples relate to lubricating compositions containing thiaadiazole.

**Example 1**

An industrial gear oil is prepared by blending 0.95 parts of 2,5- bis (tert nonylidithio) 1,3,4-thiaadiazole into an industrial gear basestock.

**Example 2**

An industrial gear oil is prepared by blending 1.2 parts of 2-mercapto, 5-tert nonylidithio- 1,3,4 thiaadiazole and 0.02 parts of as 50% solution of an ester copolymer made from ethyl acrylate and 2-ethylhexyl acrylate (100:40) into an industrial gear oil base stock.

**Example 3**

An industrial gear oil is prepared by blending 1.2 parts of the thiaadiazole from Example 1, 0.02 parts of the ester copolymer of Example 1, and 0.4 parts of the product of Example P-3.

**Example 4**

An industrial gear oil is prepared as described in Example 3, except 1.2 parts of the product of Example P-8 replaces the product of Example P-3.

**Example 5**

An industrial gear oil is prepared as described in Example 2 except that 0.05 parts of the product of Example I-2 is included in the industrial gear oil.

**Example 6**

An industrial gear oil is prepared as described in Example 4 except that 0.05 parts of the product of Example I-2 is included in the industrial gear oil.

**Example 7**

An industrial gear oil is prepared as described in Example 6 except that 0.02 parts of tolyltriazole is also included.
Example 8

An industrial gear oil is prepared as described in Example 7 except that 0.05 parts of a 40% oil solution of a dispersant (the reaction product of a polyisobutyl succinic anhydride (Mn 850) and polyethylene polyamines and having a TBN of 70) and 0.01 parts of Pluradyne FL11 (ethylene oxide-propylene oxide copolymer available from BASF).

Example 9

A manual transmission fluid is prepared by blending 1.1 parts of 2, 5- bis (tert nonylidithio) 1,3,4-thiadiazole into a manual transmission basestock.

Example 10

A manual transmission fluid is prepared by blending 1.5 parts of 2- mercapto, 5- tert nonylidithio- 1,3,4 thiadiazole and 0.01 parts of a kerosene solution of Dow Corning 200 Fluid (kinematic viscoisty of 30,000 cSt) into a manual transmission base stock.

Example 9A

A manual transmission fluid is prepared by blending 1.5 parts of 2, 5- bis (tert nonylidithio) 1,3,4-thiadiazole and 0.5 parts of the product of Example P-8 into a manual transmission basestock.

Example 10B

A manual transmission fluid is prepared as described in Example 9 except that 0.01 parts of a kerosene solution of Dow Corning 200 Fluid (kinematic viscoisty of 30,000 cSt) is also included into a manual transmission fluid.

Example 11

A manual transmission fluid is prepared as described in Example 10 except that 0.5% of dinonyldiphenyl amine is also included in the manual transmission fluid.

Example 12

A manual transmission fluid is prepared as described in Example 11 except that 1.5 parts of a 42% oil solution of overbased calcium substituted benzenesulfonate (300 TBN, 12% calcium, and 40.8% sulfated ash) is also included.

Example 13

A manual transmission fluid is prepared as described in Example 12 except that 1 part of a 50% oil solution of a dispersant (the reaction product of a
polyisobutenyl succinic anhydride (Mn 1500) and polyethylene polyamines and having a TBN of 27) is also included.

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


Claims

3090R

1. A lubricating composition comprising a major amount of an oil of lubricating viscosity and at least about 0.4% by weight of at least one amine free thia diazole, wherein the lubricating composition is free of organic polysulfides and contains less than about 2% by weight of at least one dispersant.

2. The composition of claim 1 further comprising at least one phosphorus antiwear agent.

3. The composition of claim 1 further comprising less than about 1.5% by weight of at least one dispersant and at least one anti-foam agent, and at least one imidazoline or reaction product of at least one fatty carboxylic acid and at least one polyamine, and wherein the amine free thia diazole is a mercaptothia diazole with at least one hydrocarbyl or bis-hydrocarbyl substituted thio or di thi othia dia zole.

4. An industrial gear oil composition comprising a major amount of an oil of lubricating viscosity and at least about 0.4% of at least one amine-free thia diazole and at least one phosphorus antiwear agent, wherein the lubricant is free of polysulfide compounds.

5. The composition of claim 4 wherein the composition further comprises less that about 2% by weight of at least one dispersant.

6. The composition of claim 4 wherein the composition further comprises at least one imidazoline or reaction product of at least one fatty carboxylic acid and at least one polyamine.

7. An manual transmission composition comprising a major amount of an oil of lubricating viscosity and at least about 0.4% of at least one amine-free thia diazole, wherein the lubricant is free of organic polysulfides and contains less than about 2% by weight of at least one dispersant.
8. The composition of claim 7 further comprising at least one phosphorus antiwear agent.

9. The composition of claim 7 further comprising at least one imidazoline or reaction product of at least one fatty carboxylic acid and at least one polyamine.

10. The composition of claim 7 further comprising at least one overbased metal salt of an acidic organic compound, at least one antioxidant, and at least one antifoam agent.