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54 **Lubricants and functional fluids having enhanced foam-inhibiting properties.**

57 Enhanced foam-inhibition properties result from a lubricant or functional fluid composition which comprises a base oil of lubricating viscosity having included therein a foam-inhibiting amount of a combination of (i) up to 50 ppm of a silicone oil having a viscosity above 1000 cP at 20 °C, and (ii) up to 25 ppm of metal as alkali and/or alkaline earth metal phenate.

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This invention relates to oleaginous compositions (i.e., lubricants and functional fluids) having enhanced foam-inhibiting properties.

It is recognized that certain uses of a lubricant or a functional fluid occur under conditions that tend to promote the foaming of the lubricant or functional fluid, with consequent decrease in its effectiveness.

5 Various agents which have heretofore been used to decrease foaming are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176). However, there is always a need for new, highly effective foam-inhibition materials and systems.

10 One standard test procedure used in qualifying oleaginous fluids for certification is the Turbo Hydraulic Cycling Test, which forms part of the Dexron®-II procedures. This test severely stresses the foaming tendencies of the test fluid. In practice, many fluid formulations have failed this test because of extensive foaming. Thus there is a need for a new, effective foam inhibitor composition capable of giving good performance in foam suppression, particularly in such applications as the Turbo Hydra-matic Cycling Test referred to above.

15 The present invention provides a composition promoting decreased foaming in a lubricant or functional fluid normally susceptible to foaming when in use under its usual operating conditions.

In accordance with this invention, it has now been discovered that enhanced foam-inhibition properties result from a lubricant or functional fluid composition which comprises a base oil of lubricating viscosity having included therein a foam-inhibiting amount of a combination of (i) up to 50 ppm of a silicone oil having a viscosity above 1000 cP at 20 °C, and (ii) up to 25 ppm of metal as alkali and/or alkaline earth metal phenate.

20 In accordance with one embodiment of this invention, the silicone oil has a viscosity in the range of 10,000 to 60,000 cP at 20 °C.

Another embodiment of this invention provides a composition wherein the base oil also has included therein at least one ashless dispersant or at least one antiwear/extreme pressure agent or a combination thereof. In another embodiment of this invention, the metal of component (ii) is the only metal component included in the composition. Still another embodiment provides a composition wherein the base oil also has included therein at least one antioxidant or at least one rust inhibitor or a combination thereof.

25 Yet another embodiment of this invention is the method of inhibiting foaming in an oil of lubricating viscosity during usage of such oil as a lubricant or functional fluid, which method comprises including in said oil a foam-inhibiting amount of a combination of (i) up to 50 ppm of a silicone oil having a viscosity above 1000 cP at 20 °C, and (ii) up to 25 ppm of metal as alkali and/or alkaline earth metal phenate.

30 The above and other embodiments and features of this invention will be apparent from a consideration of the detailed description below.

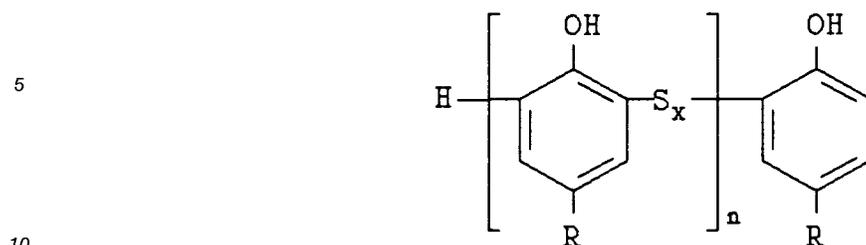
The base oils used in this invention can be not only hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes any or all of the foregoing.

35 Suitable silicone oils to be used as component (i) in the compositions of this invention include hydrocarbyl silicone oils which have a viscosity above 1000 cP at 20 °C. Preferably a dialkyl silicone oil (most preferably a dimethyl silicone oil) is used wherein the viscosity is in the range of 10,000 to 60,000 cP at 20 °C. The amount of silicone oil in the compositions of this invention is up to about 50 ppm (parts per million by weight); preferred amounts are in the range of 5 to 40 ppm.

40 The alkali or alkaline earth metal phenates which are suitable for use as component (ii) in the compositions of this invention include phenates of lithium, sodium, potassium, magnesium, calcium, barium, and the like. (Rubidium, cesium, and strontium phenates are also suitable, but their expense renders them impracticable for most uses; phenates of barium are less preferred due to the toxicological status of barium as a heavy metal.) The preferred phenates are the alkaline earth phenates, and of these, magnesium and calcium phenates are particularly preferred. The amount of metal phenate in the compositions of this invention provides up to about 25 ppm (parts per million by weight) of metal. Especially preferred are metal phenates derived from sulfurized phenols.

45 Metal phenates, and in particular, sulfurized metal phenates, have been long employed as detergents in lubricants. See, for example, U.S. 2,415,833; U.S. 2,680,096; U.S. 2,680,097; U.S. 2,916,454; U.S. 2,989,466; U.S. 3,178,368; U.S. 3,367,867; U.S. 3,801,507; U.S. 4,867,890; and others. Sulfurized metal phenates can be considered as the metal salt of a phenol sulfide, where phenol sulfide refers to a compound represented by a formula such as the following, where $x = 1$ or 2 and $n = 1, 2, \text{ or } 3$, or a polymeric form where x and n

are integers from 1 to 4 and 1 to 6 respectively:



In the above, where R is an alkyl group, the average number of carbon atoms in all of the R groups is large enough to ensure adequate solubility in oil, at least about 9. Each individual R group may contain from 5 to 40, preferably 8 to 20, carbon atoms. Useful sulfurized alkylphenols contain from about 2 to 14 wt%, preferably about 4 to 12 wt% sulfur, based on the weight of sulfurized alkylphenol. The metal phenate is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal-containing material, such as metal oxides, hydroxides, and complexes, to effect the desired reaction, i.e., to neutralize the phenol or, if desired, to "overbase" the phenate to a desired alkalinity. One such process of neutralization utilizes a solution of metal in a glycol ether. Neutral or normal sulfurized metal phenates are those in which the ratio of metal to phenol nucleus is about the stoichiometric ratio, i.e., for alkaline earth metals, about 1:2. The "over-based" sulfurized metal phenates are those in which the ratio of metal to phenol is greater than that of stoichiometry. The best results in the present invention result from use of phenates which have a TBN (Total base number) not in excess of about 250, as determined by the ASTM D-2896 test procedure.

It is contemplated that the compositions of this invention will include other additive components or packages as desired in order to confer certain properties appropriate for the specific application or use of the lubricant or functional fluid. Such other additives include, but are not limited to, detergents, dispersants, viscosity index improvers, pour point depressants, antiwear additives, extreme pressure agents, corrosion inhibitors, antioxidants, rust inhibitors, friction modifiers, seal swell agents, demulsifiers, etc., provided, of course, that the presence of such other additives in the compositions does not significantly interfere with the benefits provided by the present invention.

Metal-Containing Sulfonate Detergents. For some applications such as crankcase lubricants for diesel engines, it is desirable to include an oil-soluble metal-containing sulfonate detergent in which the metal is an alkali metal or an alkaline earth metal. Combinations of such detergents can also be employed. The neutral detergents of this type are those which contain an essentially stoichiometric equivalent quantity of metal in relation to the amount of acidic moieties present in the detergent. Thus in general, the neutral detergents will have a TBN of up to about 50. On the other hand, overbased detergents have a TBN above about 50, as they contain an amount of metal above the stoichiometric equivalent in relation to the amount of acidic moieties present in the detergent. Thus products having a TBN of up to and above 300 are feasible. The acidic materials utilized in forming such detergents include aliphatic sulfonic acids, naphthenic sulfonic acids, and preferably alkyl benzene sulfonic acids. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. Typical detergents of this type and/or methods for their preparation are known and reported in the literature. See for example U.S. Pat. Nos. 2,001,108; 2,081,075; 2,095,538; 2,144,078; 2,163,622; 2,180,697; 2,180,698; 2,180,699; 2,211,972; 2,223,127; 2,228,654; 2,228,661; 2,249,626; 2,252,793; 2,270,183; 2,281,824; 2,289,795; 2,292,205; 2,294,145; 2,321,463; 2,322,307; 2,335,017; 2,336,074; 2,339,692; 2,356,043; 2,360,302; 2,362,291; 2,399,877; 2,399,878; 2,409,687; and 2,416,281. A number of such compounds are available as articles of commerce, such as for example, HiTEC® 614 additive and HiTEC® 611 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Limited).

Ashless dispersants. Any of a variety of ashless dispersants can be utilized in the compositions of this invention. These include the following types:

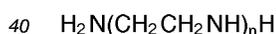
Type A - Carboxylic Ashless Dispersants. These are reaction products of an acylating agent (e.g., a monocarboxylic acid, dicarboxylic acid, polycarboxylic acid, or derivatives thereof) with one or more polyamines and/or polyhydroxy compounds. These products, herein referred to as carboxylic ashless dispersants, are described in many patents, including British Patent Specification 1,306,529 and the following U. S. Patents: 3,163,603; 3,184,474; 3,215,707; 3,219,666; 3,271,310; 3,272,746; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,340,281; 3,341,542; 3,346,493; 3,381,022; 3,399,141; 3,415,750; 3,433,744; 3,444,170; 3,448,048; 3,448,049; 3,451,933; 3,454,607; 3,467,668; 3,522,179; 3,541,012;

3,542,678; 3,574,101; 3,576,743; 3,630,904; 3,632,510; 3,632,511; 3,697,428; 3,725,441; 3,868,330; 3,948,800; 4,234,435; and Re 26,433.

There are a number of sub-categories of carboxylic ashless dispersants. One such sub-category which constitutes a preferred type for use in the formation of component b) is composed of the polyamine succinamides and more preferably the polyamine succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms. The polyamine used in forming such compounds contains at least one primary amino group capable of forming an imide group on reaction with a hydrocarbon-substituted succinic acid or acid derivative thereof such as an anhydride, lower alkyl ester, acid halide, or acid-ester. Representative examples of such dispersants are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to about 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, 1-butene, isobutene and the like. The more preferred source of alkenyl group is from polyisobutene having a number average molecular weight of up to 100,000 or higher. In a still more preferred embodiment the alkenyl group is a polyisobutenyl group having a number average molecular weight (determined using the method described in detail hereinafter) of about 500-5,000, and preferably about 700-2,500, more preferably about 700-1,400, and especially 800-1,200. The isobutene used in making the polyisobutene is usually (but not necessarily) a mixture of isobutene and other C₄ isomers such as 1-butene. Thus, strictly speaking, the acylating agent formed from maleic anhydride and "polyisobutene" made from such mixtures of isobutene and other C₄ isomers such as 1-butene, can be termed a "polybutenyl succinic anhydride" and a succinimide made therewith can be termed a "polybutenyl succinimide". However, it is common to refer to such substances as "polyisobutenyl succinic anhydride" and "polyisobutenyl succinimide", respectively. As used herein "polyisobutenyl" is used to denote the alkenyl moiety whether made from a highly pure isobutene or a more impure mixture of isobutene and other C₄ isomers such as 1-butene.

Polyamines which may be employed in forming the ashless dispersant include any that have at least one primary amino group which can react to form an imide group. A few representative examples include branched-chain alkanes containing two or more primary amino groups such as tetraamino-neopentane, etc.; polyaminoalkanols such as 2-(2-aminoethylamino)-ethanol and 2-[2-(2-aminoethylamino)-ethylamino]-ethanol; heterocyclic compounds containing two or more amino groups at least one of which is a primary amino group such as 1-(β-aminoethyl)-2-imidazolidone, 2-(2-aminoethylamino)-5-nitropyridine, 3-amino-N-ethylpiperidine, 2-(2-aminoethyl)-pyridine, 5-aminoindole, 3-amino-5-mercapto-1,2,4-triazole, and 4-(aminomethyl)-piperidine; and the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, N-(2-aminoethyl)-1,3-propanediamine, hexamethylenediamine and tetra-(1,2-propylene)pentamine.

The most preferred amines are the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, N,N'-bis(piperaziny)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred. Methods for the production of polyalkylene polyamines are known and reported in the literature. See for example U.S. Pat. No. 4,827,037 and references cited therein.

Thus especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon-substituted carboxylic acid or anhydride (or other suitable acid derivative) made by reaction of a polyolefin, preferably polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400 and especially 800 to 1,200, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including

mixtures of two or more such substances.

As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between the amine reactant(s) and the hydrocarbon-substituted carboxylic acid or anhydride (or like acid derivative) reactant(s), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Residual unsaturation in the alkenyl group of the alkenyl succinimide may be used as a reaction site, if desired. For example the alkenyl substituent may be hydrogenated to form an alkyl substituent. Similarly the olefinic bond(s) in the alkenyl substituent may be sulfurized, halogenated, hydrohalogenated or the like. Ordinarily, there is little to be gained by use of such techniques, and thus the use of alkenyl succinimides as the precursor of component b) is preferred.

Another sub-category of carboxylic ashless dispersants which can be used in the compositions of this invention includes alkenyl succinic acid esters and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above including the same preferred and most preferred subgenus, e.g., alkenyl succinic acids and anhydrides, etc., where the alkenyl group contains at least 30 carbon atoms and notably, polyisobutenyl succinic acids and anhydrides wherein the polyisobutenyl group has a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. As in the case of the succinimides, the alkenyl group can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Alcohols useful in preparing the esters include methanol, ethanol, 2-methylpropanol, octadecanol, eicosanol, ethylene glycol, diethylene glycol, tetraethylene glycol, diethylene glycol monoethylether, propylene glycol, tripropylene glycol, glycerol, sorbitol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 1,1,1-trimethylolbutane, pentaerythritol, dipentaerythritol, and the like.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C₁-C₄) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydrides can be merely reacted with an appropriate alkylene oxide such as ethylene oxide, propylene oxide, and the like, including mixtures thereof.

Still another sub-category of carboxylic ashless dispersants useful in forming compositions of this invention comprises an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters or etc. with an alcohol and an amine either sequentially or in a mixture. The alcohols and amines described above are also useful in this embodiment. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 1-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms. Examples are ethanolamine, diethanolamine, N-ethanol-diethylene triamine, and trimethylol aminomethane.

Here again, the alkenyl group of the succinic ester-amide can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Representative examples of suitable ester-amide mixtures are referred to in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

Yet another sub-category of carboxylic ashless dispersants which can be used comprises the Mannich-based derivatives of hydroxyaryl succinimides. Such compounds can be made by reacting a polyalkenyl succinic anhydride with an aminophenol to produce an N-(hydroxyaryl) hydrocarbyl succinimide which is then reacted with an alkylene diamine or polyalkylene polyamine and an aldehyde (e.g., formaldehyde), in a Mannich-base reaction. Details of such synthesis are set forth in U.S. Pat. No. 4,354,950. As in the case of the other carboxylic ashless dispersants discussed above, the alkenyl succinic anhydride or like acylating agent is derived from a polyolefin, preferably a polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. Likewise, residual unsaturation in the polyalkenyl substituent group can be used as a reaction site as for example, by hydrogenation, sulfurization, or the like.

Type B - Mannich polyamine dispersants. This category of ashless dispersant which can be utilized in the compositions of this invention is comprised of reaction products of an alkyl phenol, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines of the type described hereinabove). Examples of these Mannich polyamine dispersants are described in the following U.S. Patents: 2,459,112; 2,962,442;

2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,980,569; and 4,011,380.

5 The polyamine group of the Mannich polyamine dispersants is derived from polyamine compounds characterized by containing a group of the structure -NH- wherein the two remaining valences of the nitrogen are satisfied by hydrogen, amino, or organic radicals bonded to said nitrogen atom. These compounds include aliphatic, aromatic, heterocyclic and carbocyclic polyamines. The source of the oil-soluble hydrocarbyl group in the Mannich polyamine dispersant is a hydrocarbyl-substituted hydroxy aromatic compound comprising the reaction product of a hydroxy aromatic compound, according to well known procedures, with a hydrocarbyl donating agent or hydrocarbon source. The hydrocarbyl substituent provides substantial oil solubility to the hydroxy aromatic compound and, preferably, is substantially aliphatic in character. Commonly, the hydrocarbyl substituent is derived from a polyolefin having at least about 40 carbon atoms. The hydrocarbon source should be substantially free from pendant groups which render the hydrocarbyl group oil insoluble. Examples of acceptable substituent groups are halide, hydroxy, ether, carboxy, ester, amide, nitro and cyano. However, these substituent groups preferably comprise no more than about 10 weight percent of the hydrocarbon source.

10 The preferred hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from substantially saturated petroleum fractions and olefin polymers, preferably polymers of mono-olefins having from 2 to about 30 carbon atoms. The hydrocarbon source can be derived, for example, from polymers of olefins such as ethylene, propene, 1-butene, isobutene, 1-octene, 1-methylcyclohexene, 2-butene and 3-pentene. Also useful are copolymers of such olefins with other polymerizable olefinic substances such as styrene. In general, these copolymers should contain at least 80 percent and preferably about 95 percent, on a weight basis, of units derived from the aliphatic mono-olefins to preserve oil solubility. The hydrocarbon source generally contains at least about 40 and preferably at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a number average molecular weight between about 600 and 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers.

20 25 30 35 The Mannich polyamine dispersants are generally prepared by reacting a hydrocarbyl-substituted hydroxy aromatic compound with an aldehyde and a polyamine. Typically, the substituted hydroxy aromatic compound is contacted with from about 0.1 to about 10 moles of polyamine and about 0.1 to about 10 moles of aldehyde per mole of substituted hydroxy aromatic compound. The reactants are mixed and heated to a temperature above about 80 °C. to initiate the reaction. Preferably, the reaction is carried out at a temperature from about 100 ° to about 250 °C. The resulting Mannich product has a predominantly benzylamine linkage between the aromatic compound and the polyamine. The reaction can be carried out in an inert diluent such as mineral oil, benzene, toluene, naphtha, ligroin, or other inert solvents to facilitate control of viscosity, temperature and reaction rate.

40 45 Suitable polyamines for use in preparation of the Mannich polyamine dispersants include, but are not limited to, methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines and heptylene polyamines. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also useful. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)amine, propylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, decamethylene diamine, di(heptamethylene) triamine, pentaethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2-aminopropyl)imidazoline, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs, obtained by condensing two or more of the above mentioned amines, are also useful, as are the polyoxyalkylene polyamines.

50 55 The polyalkylene polyamines, examples of which are set forth above, are especially useful in preparing the Mannich polyamine dispersants for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of somewhat complex mixtures of polyalkylene polyamines which include cyclic condensation products such as piperazines. Because of their availability, these mixtures are particularly useful in preparing the Mannich polyamine dispersants. However, it will be appreciated that satisfactory dispersants can also be obtained by use of pure polyalkylene polyamines.

Alkylene diamines and polyalkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atom are also useful in preparing the Mannich polyamine dispersants. These materials are typically obtained by reaction of the corresponding polyamine with an epoxide such as ethylene oxide or propylene oxide. Preferred hydroxyalkyl-substituted diamines and polyamines are those in which the hydroxyalkyl groups have less than about 10 carbon atoms. Examples of suitable hydroxyalkyl-substituted diamines and polyamines include, but are not limited to, N-(2-hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxyethyl)ethylenediamine, mono(hydroxypropyl)diethylenetriamine, di(hydroxypropyl)tetraethylenepentamine and N-(3-hydroxybutyl)tetramethylenediamine. Higher homologs obtained by condensation of the above mentioned hydroxyalkyl-substituted diamines and polyamines through amine groups or through ether groups are also useful.

Any conventional formaldehyde yielding reagent is useful for the preparation of the Mannich polyamine dispersants. Examples of such formaldehyde yielding reagents are trioxane, paraformaldehyde, trioxymethylene, aqueous formalin and gaseous formaldehyde.

Type C - Polymeric polyamine dispersants. Also suitable for use in the compositions of this invention are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such polymeric dispersants are herein referred to as polymeric polyamine dispersants. Such materials include, but are not limited to, interpolymers of decyl methacrylate, vinyl decyl ether or a relatively high molecular weight olefin with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in the following patents: U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; 3,702,300.

Type D - Post-treated ashless dispersants. Any of the ashless dispersants referred to above as types A-C can be subjected to post-treatment with one or more suitable reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, anhydrides of low molecular weight dibasic acids, nitriles, epoxides, phosphorus acids, phosphorus esters, boron acids, boron esters, boron oxides, and the like. Such post-treated ashless dispersants can be used in forming the compositions of this invention. Examples of post-treatment procedures and post-treated ashless dispersants are set forth in the following U.S. Patents: U.S. Pat. Nos. 3,036,003; 3,200,107; 3,216,936; 3,256,185; 3,278,550; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,702,757; and 3,708,522; and 4,971,598.

Mannich-based derivatives of hydroxyaryl succinimides that have been post-treated with C₅-C₉ lactones such as ϵ -caprolactone and optionally with other post-treating agents as described for example in U.S. Pat. No. 4,971,711 can also be utilized in the practice of this invention. See also U.S. Pat. No. 4,971,711, as well as related U.S. Pat. Nos. 4,820,432; 4,828,742; 4,866,135; 4,866,139; 4,866,140; 4,866,141; 4,866,142; 4,906,394; and 4,913,830 as regards additional suitable ashless dispersants which may be utilized.

Viscosity index improvers. Suitable viscosity index improvers for inclusion in the compositions of this invention include such materials as polymethacrylate polymers, polyalkylmethacrylate polymers, polyacrylate polymers, styrene-maleic ester copolymers, ethylene-propylene copolymers, styrene-diene copolymers, styrene-diene copolymers, and similar polymeric substances including homopolymers, copolymers, and graft copolymers.

Pour Point Depressants. Another useful type of additive included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the books *Lubricant Additives* by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967); *Gear and Transmission Lubricants* by C. T. Boner (Reinhold Publishing Corp., New York, 1964); and *Lubricant Additives* by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973). Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715.

Active-sulfur-containing antiwear and/or extreme pressure agents. Typical active-sulfur-containing antiwear and/or extreme pressure additives include dihydrocarbyl polysulfides; sulfurized olefins; sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins; trithiones; sulfurized thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C₂-C₈ monoolefins; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331, the disclosure of which is incorporated herein by reference. Specific examples include sulfurized polyisobutene of \bar{M}_n 1,100, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl polysulfide, diphenyl and dibenzyl polysulfide, di-tert-butyl polysulfide, and dinonyl polysulfide, among others.

Phosphorus-containing antiwear and/or extreme pressure agents. Generally speaking there are two principal categories of phosphorus-containing antiwear and/or extreme pressure agents: metal salts of phosphorus acids, and metal-free phosphorus compounds. The metal salts are the oil-soluble salts of a metal such as copper, cadmium, calcium, magnesium, and most notably, zinc, and of a suitable acidic compound of phosphorus, such as a thiophosphoric acid, a dithiophosphoric acid, a trithiophosphoric acid, a tetrathiophosphoric acid or of a complex acidic product formed by phosphosulfurizing a hydrocarbon such as one or more olefins or terpenes with a reactant such as phosphorus pentasulfide and hydrolyzing the resultant product. Methods of forming such metal salts are well known to those skilled in the art and are extensively described in the patent literature.

The oil-soluble metal-free phosphorus-containing antiwear and/or extreme pressure agents are for the most part partially or fully esterified acids of phosphorus. Such compounds include for example phosphates, phosphites, phosphonates, phosphonites, and their various sulfur analogs. Examples include monohydrocarbyl phosphites; monohydrocarbyl phosphates; monohydrocarbyl mono-, di-, tri-, and tetrathiophosphites; monohydrocarbyl mono-, di-, tri-, and tetrathiophosphates; dihydrocarbyl phosphites; dihydrocarbyl phosphates; dihydrocarbyl mono-, di-, tri-, and tetrathiophosphites; dihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; trihydrocarbyl phosphites; trihydrocarbyl phosphates; trihydrocarbyl mono-, di-, tri-, and tetrathiophosphites; trihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; the various hydrocarbyl phosphonates and thiophosphonates; the various hydrocarbyl phosphonites and thiophosphonites, and analogous oil-soluble derivatives of polyphosphoric and polythiophosphoric acids; and many others. A few specific examples of such compounds are tricresyl phosphate, tributyl phosphite, triphenyl phosphite, tri-(2-ethylhexyl) phosphate, dihexyl thiophosphite, diisooctyl butylphosphonate, tricyclohexyl phosphate, cresyl diphenyl phosphate, tris(2-butoxyethyl) phosphite, diisopropyl dithiophosphate, tris(tridecyl)-tetrathiophosphate, tris(2-chloroethyl) phosphate, and like compounds.

Preferred ashless (i.e., metal-free) phosphorus-containing antiwear and/or extreme pressure agents for use in the practice of this invention are (a) the oil-soluble amine salts of monohydrocarbyl monothiophosphoric acids, (b) the oil-soluble amine salts of dihydrocarbyl monothiophosphoric acids, and (c) combinations of (a) and (b). Such compounds can be made by reacting a mono- and/or dihydrocarbyl phosphite with sulfur or an active sulfur-containing compound such as are referred to above under the caption "Active-sulfur-containing antiwear and/or extreme pressure agents" and one or more primary or secondary amines. Such reactions tend to be highly exothermic reactions which can become uncontrollable, if not conducted properly. The preferred method of forming these amine salts involves a process which comprises (i) introducing, at a rate such that the temperature does not exceed about 60 °C, one or more dihydrocarbyl hydrogen phosphites, such as a dialkyl hydrogen phosphite, into an excess quantity of one or more active-sulfur-containing materials, such as sulfurized branched-chain olefin (e.g., isobutylene, diisobutylene, triisobutylene, etc.), while agitating the mixture so formed, (ii) introducing into this mixture, at a rate such that the temperature does not exceed about 60 °C, one or more aliphatic primary or secondary amines, preferably one or more aliphatic primary monoamines having in the range of about 8 to about 24 carbon atoms per molecule while agitating the mixture so formed, and (iii) maintaining the temperature of the resultant agitated reaction mixture at between about 55 and about 60 °C until reaction is substantially complete. Another suitable way of producing these amine salts is to concurrently introduce all three of the reactants into the reaction zone at suitable rates and under temperature control such that the temperature does not exceed about 60 °C.

Copper corrosion inhibitors. One type of such additives is comprised of thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-(bis)hydrocarbyldithio-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles and the 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,749,311; 2,760,933; 2,765,289; 2,850,453; 2,910,439; 3,663,561; 3,862,798; 3,840,549; and 4,097,387.

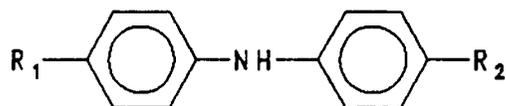
Antioxidants. Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like.

Illustrative sterically hindered phenolic antioxidants include ortho-alkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenolic compounds are also suitable.

The preferred antioxidants for use in the compositions of this invention are methylene-bridged alkylphenols, and these can be used singly or in combinations with each other, or in combinations with sterically-hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tert-butylphenol), and similar compounds. Particularly preferred are mixtures of methylene-bridged alkylphenols such as are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used in the compositions of this invention. Although aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to about 16 carbon atoms, phenyl- α -naphthylamine, phenyl- β -naphthylamine, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- β -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine of the general formula



wherein R_1 is an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms) and R_2 is a hydrogen atom or an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms). Most preferably, R_1 and R_2 are the same. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominately a 4,4'-dinonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

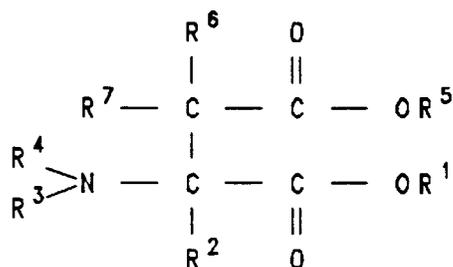
Another useful type of antioxidant for inclusion in the compositions of this invention is comprised to one or more liquid, partially sulfurized phenolic compounds such as are prepared by reacting sulfur monochloride with a liquid mixture of phenols -- at least about 50 weight percent of which mixture of phenols is composed of one or more reactive, hindered phenols -- in proportions to provide from about 0.3 to about 0.7 gram atoms of sulfur monochloride per mole of reactive, hindered phenol so as to produce a liquid product. Typical phenol mixtures useful in making such liquid product compositions include a mixture containing by weight about 75% of 2,6-di-tert-butylphenol, about 10% of 2-tert-butylphenol, about 13% of 2,4,6-tri-tert-butylphenol, and about 2% of 2,4-di-tert-butylphenol. The reaction is exothermic and thus is preferably kept within the range of about 15°C to about 70°C, most preferably between about 40°C to about 60°C.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one bis(4-alkylphenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

Corrosion or Rust Inhibitors. The compositions of this invention may also contain a suitable quantity of a corrosion or rust inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Such materials include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of corrosion inhibitor for use in the practice of

this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

Other useful corrosion inhibitors are aminosuccinic acids or derivatives thereof represented by the formula:



wherein each of R^1 , R^2 , R^5 , R^6 and R^7 is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R^3 and R^4 is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms. The groups R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 , when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R^1 and R^5 are the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R^1 and R^5 are saturated hydrocarbon radicals containing 3-6 carbon atoms. R^2 , either R^3 or R^4 , R^6 and R^7 , when in the form of hydrocarbyl groups, are preferably the same or different straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl ester of an aminosuccinic acid is used in which R^1 and R^5 are the same or different alkyl groups containing 3-6 carbon atoms, R^2 is a hydrogen atom, and either R^3 or R^4 is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred of the aminosuccinic acid derivatives is a dialkylester of an aminosuccinic acid of the above formula wherein R^1 and R^5 are isobutyl, R^2 is a hydrogen atom, R^3 is octadecyl and/or octadecenyl and R^4 is 3-carboxy-1-oxo-2propenyl. In such ester R^6 and R^7 are most preferably hydrogen atoms.

Friction Modifiers. These materials include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat. 4,105,571, oleamide, and the like. Such additives, when used are generally present in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

Seal Swell Agents. Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions. Known materials of this type include dialkyl diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N, products such as Lubrizol 730, polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corp. and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corp. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C_8 - C_{13} alkanols (or mixtures thereof), and the phthalates of C_4 - C_{13} alkanols (or mixtures

thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid.

5 Demulsifiers. Typical additives which may be employed as demulsifiers include alkyl benzene sulfonates, polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, salts and esters or oil soluble acids, and the like.

Base Oils. The additive combinations of this invention can be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, 10 hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of 15 petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic 20 oils. Among the suitable synthetic oils are homo- and inter-polymers of C₂-C₁₂ olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, polyglycols, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C₂-C₁₂ monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, 25 wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl 30 polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C₃-C₆ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, 35 succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)adipate, didodecyl adipate, di(2-ethylhexyl)sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl)sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic 40 acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters which may be used as synthetic oils also include those made from C₃-C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylolpropane tripelargonate and pentaerythritol tetracaproate serve as examples.

45 Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid).

Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C₆-C₁₆ alpha-olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and 50 reported in the literature. See for example U. S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, for example, under the trade designations ETHYLFLO™ 162, ETHYLFLO™ 164, ETHYLFLO™ 166, ETHYLFLO™ 168, ETHYLFLO™ 170, ETHYLFLO™ 174, and ETHYLFLO™ 180 poly-alpha-olefin oils (Ethyl Corporation; Ethyl S.A.; Ethyl Canada Limited). Blends of such materials can also be 55 used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C₁₋₂₀ alkanol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

Proportions and Concentrations

In general, the ancillary components of the compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. The amounts will thus vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. The concentrations (weight percent of active ingredient) of typical optional ingredients in the oleaginous liquid compositions of this invention are generally as follows:

	Typical Range	Preferred Range
Metal sulfonate detergent	0 - 3	0 - 2.5
Ashless dispersant	0 - 10	0 - 5
Viscosity index improver	0 - 20	0 - 12
Pour point depressant	0 - 5	0 - 2
Antiwear/EP agent	0 - 5	0 - 2
Cu corrosion inhibitor	0 - 0.5	0.01 - 0.2
Antioxidant	0 - 4	0.05 - 2
Rust inhibitor	0 - 2	0.02 - 1
Friction modifier	0 - 3	0 - 1
Seal swell agent	0 - 20	0 - 10
Demulsifiers	0 - 1	0 - 0.2
Antioxidant	0 - 3	0.1 - 1

It will be appreciated that the individual components (i) and (ii), and also any and all auxiliary components employed, can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which are usually blended apart from other components), it is preferable to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the

overall concentrate. The additive concentrates of this invention will contain the components employed in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 50% by weight of one or more diluents or solvents can be used.

The following examples, while not limiting, serve to illustrate the practice of the present invention. In these examples all percentages are by weight.

EXAMPLE 1

Into a base oil composed of 80% refined 90 solvent neutral mineral oil and 20% refined 195 solvent neutral mineral oil are blended 0.05% calcium phenate (OLOA 216C; Chevron Chemical Co.,) and 0.06% of a 4% solution of Dow Corning silicone fluid DC-200 -- a silicone oil having a viscosity of 60,000 cP -- in a hydrocarbon solvent (Shellsol 140 or equivalent). The resultant oil is highly resistant to foam formation, more so than the same oil containing the same additives individually.

EXAMPLE 2

Example 1 is repeated except that the base oil is Exxon 1365 oil, a low pour, solvent neutral mineral oil.

EXAMPLE 3

Example 1 is repeated, but using Chevron RLOP oil, a hydrocracked 100 neutral mineral oil, as the base oil.

EXAMPLE 4

Example 1 is repeated using a 4-cSt hydrogenated poly- α -olefin oligomer -- ETHYLFLO™ 164 oligomer oil (Ethyl Corporation; Ethyl S.A.; Ethyl Canada Limited) -- as the base oil.

EXAMPLE 5

The procedure of Example 4 is repeated except that the base oil is a 6-cSt hydrogenated poly- α -olefin oligomer, namely, ETHYLFLO™ 166 oligomer oil (available from Ethyl Corporation; Ethyl S.A.; and Ethyl Canada Limited)

EXAMPLE 6

Example 1 is repeated using a synthetic diester oil as the base oil, namely, diisononyl adipate.

EXAMPLE 7

Example 6 is repeated except that the base oil is di(tridecyl)sebacate.

EXAMPLE 8

Example 6 is again repeated, but using di(tridecyl)phthalate as the base oil.

As can easily be seen above, many variations are possible within the spirit and scope of the present invention.

Claims

1. A lubricant or functional fluid composition which comprises a base oil of lubricating viscosity having included therein a foam-inhibiting amount of a combination of (i) up to 50 ppm of a silicone oil having a viscosity above 1000 cP at 20 °C, and (ii) up to 25 ppm of metal as alkali and/or alkaline earth metal phenate.

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2. A composition according to Claim 1 wherein said silicone oil has a viscosity in the range of 10,000 to 60,000 cP at 20° C.
- 5 3. A composition according to Claim 1 or 2 wherein the amount of said silicone oil is in the range of 5 to 40 ppm.
4. A composition according to any of Claims 1 to 3 wherein said silicone oil is a dimethyl silicone oil.
- 10 5. A composition according to any of Claims 1 to 4 wherein said phenate is an alkaline earth metal phenate.
6. A composition according to any of Claims 1 to 5 wherein said phenate is a calcium phenate.
- 15 7. A composition according to any of Claims 1 to 6 wherein said metal phenate is derived from a sulfurized phenol.
8. A composition according to any of Claims 1 to 7 wherein said base oil also has included therein (a) at least one ashless dispersant, (b) at least one antiwear/extreme pressure agent, or a combination of (a) and (b) hereof.
- 20 9. A composition according to any of Claims 1 to 8 wherein the metal of component (ii) is the only metal component included in the composition.
- 25 10. A composition according to any of Claims 1 to 9 wherein said base oil also has included therein (a) at least one antioxidant, (b) at least one rust inhibitor, or a combination of (a) and (b) hereof.
- 30 11. A method of inhibiting foaming in an oil of lubricating viscosity during usage of such oil as a lubricant or functional fluid, which method comprises including in said oil a foam-inhibiting amount of a combination of (i) up to 50 ppm of a silicone oil having a viscosity above 1000 cP at 20° C, and (ii) up to 25 ppm of metal as alkali and/or alkaline earth metal phenate, such that said lubricant or functional fluid is in accordance with any of Claims 1 to 10.
- 35 12. The use of an oil containing a combination of (i) and (ii) as set forth in any of Claims 1 to 7.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 7806

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-2 972 579 (DELFEL) * the whole document *	1, 3-7, 11, 12	C10M161/00 C10M169/04
Y	---	2	
Y	US-A-3 213 024 (BLAKE ET AL.) * column 8, line 47 *	2	
X	EP-A-0 037 186 (EXXON) * the whole document *	1, 4-6, 8, 10-12	
X	US-A-3 436 348 (CHAO ET AL.) * column 1 - column 5; claims 1, 17 * * column 7, line 60 *	1, 3, 4, 8, 10-12	
X	CH-A-587 339 (TENNECO CHEMICALS) * the whole document *	1, 3-6, 8, 10-12	
X	US-A-4 131 551 (THOMPSON ET AL.) * the whole document *	1, 3-8, 10-12	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C10M
A	US-A-3 450 636 (RAUSCH) * the whole document *	1-12	
A	US-A-2 435 124 (BOLLINGER) * the whole document *	1-12	
A	US-A-2 993 856 (HEISIG ET AL.) * the whole document *	1-12	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 MAY 1992	Examiner OE LA MORINERIE
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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