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(54) LUBRICATING OIL COMPOSITIONS AND CONCENTRATES.

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EP 0 433 409 B1

DescriptionField of the Invention

5 This invention relates to lubricating oil compositions. In particular, this invention relates to lubricating oil compositions exhibiting improved oxidation and wear performance.

Background of the Invention

10 Lubricating oils which are utilized in internal combustion engines, and in particular, in spark-ignited and diesel engines are constantly being modified and improved to provide improved performance. Various organizations including the SAE (Society of Automotive Engineers), the ASTM (formerly the American Society for Testing and Materials) and the API (American Petroleum Institute) as well as the automotive manufacturers continually seek to improve the performance of lubricating oils. Various standards have been
 15 established and modified over the years through the efforts of these organizations. As engines have increased in power output and complexity, the performance requirements have been increased to provide lubricating oils that will exhibit a reduced tendency to deteriorate under conditions of use and thereby to reduce wear and the formation of such undesirable deposits as varnish, sludge, carbonaceous materials and resinous materials which tend to adhere to the various engine parts and reduce the efficiency of the
 20 engines.

In general, different classifications of oils and performance requirements have been established for crankcase lubricants to be used in spark-ignited and diesel engines because of the differences in/and the demands placed on, lubricating oils in these applications. Until recently, high quality commercially available quality oils designed for spark-ignition engines were identified and labeled as "SF" oils. These oils are
 25 capable of satisfying the performance requirements of API Service Classification SF. A new API Service Classification SG has now been established, and this oil is to be labeled "SG". The oils designated as SG must pass the performance requirements of API Service Classification SG which have been established to insure that these new oils will possess additional desirable properties and performance capabilities in excess of those required for SF oils. The SG oils are designed to minimize engine wear and deposits and
 30 also to minimize lubricant thickening in service. The SG oils are intended to improve engine performance and durability when compared to all previous engine oils marketed for spark-ignition engines. An added feature of SG oils is the inclusion of the requirements of the API Service Classification CC category (diesel) into the SG specification.

In order to meet the performance requirements of SG oils, the oils must successfully pass the following
 35 gasoline and diesel engine tests which have been established as standards in the industry: The Ford Sequence VE Test; The Buick Sequence IIIE Test; The Oldsmobile Sequence IID Test; The CRC L-38 Test; and The Caterpillar Single Cylinder Test Engine 1H2. The Caterpillar Test is included in the performance requirements in order to also qualify the oil for the light duty diesel use (diesel performance category "CC"). If it is desired to have the SG classification oil also qualify for heavy duty diesel use, (diesel category "CD")
 40 the oil formulation must pass the more stringent performance requirements of the Caterpillar Single Cylinder Test Engine 1G2. The procedures and performance criteria for all of these tests have been established by the industry, and the tests are described in more detail below.

When it is desired that the lubricating oils of the SG classification also exhibit improved fuel economy, the oil must meet the requirements of the Sequence VI Fuel Efficient Engine Oil Dynamometer Test.

45 A new classification of diesel engine oil also has been established through the joint efforts of the SAE, ASTM and the API, and the new diesel oils will be labeled "CE". The oils meeting the new diesel classification CE will have to be capable of meeting additional performance requirements not found in the present CD category including the Mack T-6, Mack T-7, and the Cummins NTC-400 Tests.

An ideal lubricant for most purposes should possess the same viscosity at all temperatures. Available
 50 lubricants, however, depart from this ideal. Materials which have been added to lubricants to minimize the viscosity change with temperature are called viscosity-modifiers, viscosity-improvers, viscosity-index-improvers or VI improvers. In general, the materials which improve the VI characteristics of lubricating oils are oil soluble organic polymers, and these polymers include polyisobutylenes, polymethacrylates (i.e., copolymers of various chain length alkyl methacrylates); copolymers of ethylene and propylene; hydroge-
 55 nated block copolymers of styrene and isoprene; and polyacrylates (i.e., copolymers of various chain length alkyl acrylates).

Other materials have been included in the lubricating oil compositions to enable the oil compositions to meet the various performance requirements, and these include dispersants, detergents, friction modifiers,

corrosion-inhibitors, etc. Dispersants are employed in lubricants to maintain impurities in suspension, particularly those formed during operation of an internal combustion engine, rather than allowing them to deposit as sludge. Materials have been described in the prior art which exhibit both viscosity-improving and dispersant properties. One type of compound having both properties is comprised of a polymer backbone
 5 onto which backbone has been attached one or more monomers having polar groups. Such compounds are frequently prepared by a grafting operation wherein the backbone polymer is reacted directly with a suitable monomer.

Dispersant additives for lubricants comprising the reaction products of hydroxy compounds or amines with substituted succinic acids or their derivatives also have been described in the prior art, and typical
 10 dispersants of this type are disclosed in, for example, U.S. Patents 3,272,746; 3,522,179; 3,219,666; and 4,234,435. When incorporated into lubricating oils, the compositions described in the '435 patent function as dispersants/detergents and viscosity-index improvers.

Lubricating oil compositions containing oil-soluble transition metal-containing compounds also have been described in the prior art. The transition metal compounds often are salts of acidic materials such as
 15 carboxylic acids, sulfonic acids, or mixtures thereof. For example, U.S. Patent 4,162,986 (Alkaitis et al) describes transition metal salts of mixed organic carboxylic and sulfonic or second carboxylic acids and their use as lubricant additives. The transition metal compounds are also suggested as being useful as catalysts, anti-knock agents, combustion improvers, smoke suppressants, curing agents, driers, micro-nutrient sources, etc. Hydrolyzable manganese soaps which are stabilized by the inclusion of propionic acid
 20 are described as useful in greases, lubricating oils, fuels, etc. in U.S. Patent 3,762,890 (Collins).

Other patents and publications suggesting the use of various manganese salts and compounds as additives in lubricating oil compositions include, for example, U.S. Patents 2,364,283 (Freuler); 2,378,820 (Amott); 2,389,527 (McCleary); 3,346,493 (LeSuer); 3,827,979 (Piotrowski et al); 4,252,659 (Ali); 4,505,718 (Dorer); 4,633,001 (Cells); 4,664,677 (Dorer et al); European Patent Application 0271363; and European
 25 Patent Application 0,290,457. U.S. Patent 3,941,606 (Collins et al) describes hydrocarbon-soluble compositions comprising the reaction product of a polyvalent metal (e.g., Mn, Co and Ni) or polyvalent metal derivative (e.g., MnO, CoO and NiO) with a mixture comprising at least one acidic compound (e.g., fatty acids) and at least one polyhydroxy compound. The compositions are described as useful as siccatives in paint and similar coating drier compositions, fuel additives, and stabilizers for plastics.

U.S. Patent 4,505,718 and EP 0,290,457 describe hydrocarbon-soluble compositions which comprise
 30 one or more transition metal salts of at least one organic carboxylic acid, and at least one hydrocarbon-soluble ashless dispersant. The transition metal salts described in these patents include manganese salts of organic acids including carboxylic acids, sulfonic acids and phosphorus acids. A preference is expressed for overbased transition metal salts including manganese salts of the organic acids. Overbased metal salts
 35 are defined in the art and herein as salts in which the metal is present in excess of the stoichiometric amount required to react with the acidic groups of the organic acids. A larger number of ashless dispersants are disclosed as being useful in combination with the transition metal salts. References are included to many patents and several textbook publications describing ashless dispersants. Acylated nitrogen-containing dispersants are included in the types of dispersants utilized in the lubricant compositions. U.S. Patent
 40 4,505,718 describes lubricating oil compositions containing from 1 to about 500 ppm of the transition metal (as metal) and about 5 to about 1000 ppm by weight of ashless dispersant.

U.S. Patent 4,664,677 describes compositions comprising a mixture of manganese salts and copper salts. The compositions are described as being useful in fuel compositions. Fuels containing the copper and manganese compositions are disclosed as being useful for reducing the ignition temperature of exhaust
 45 particulate from diesel engines when operated using the described fuel compositions.

European Patent Publication 271363 describes oil-soluble compositions which contain a dispersant material, a detergent material, a zinc dihydrocarbyl dithiophosphate anti-wear material, and a compatibilizing material which comprises a metal salt of a hydrocarbyl-substituted mono- or dicarboxylic acid. A number of dispersants are described including those based on long chain hydrocarbyl-substituted mono- or dicarboxylic acid materials such as long chain hydrocarbons, generally polyolefin-substituted with an alpha- or beta-unsaturated dicarboxylic acid. The dispersants generally contain at least about 1.05 moles (e.g., 1.05 to 1.2 moles, or higher) of the acid per mole of polyolefin. The olefin polymers usually have a number average molecular weight of above 700 including number average molecular weights within the range of from 1500 to 5000. Polyisobutylene is described as an especially suitable starting material. The dispersants are
 50 obtained by reacting the dicarboxylic acid materials with amines, alcohols, amino alcohols, etc. The metal salts suitable as compatibilizing materials include salts of metals from Groups Ib, IIb, IIIb, IVb, Vb, VIb, VIIb and VIII of the Periodic Table. Preferred metals are from Groups Ib and IIb, and the most preferred metal is copper. The salts may be basic, neutral or acidic, and they may be formed by reacting the reactive metal
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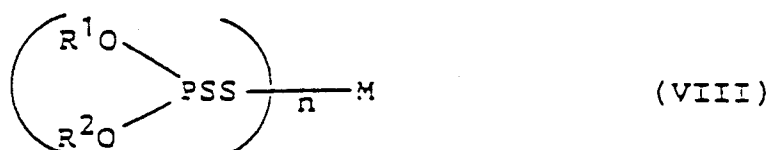
compound with any of the materials described as being dispersant materials which have at least one free carboxylic acid group. Specific examples of compatibilizing materials include the copper and zinc salts of polyisobutenyl succinic anhydride.

5 Summary of the Invention

A lubricating oil composition is described which is useful in internal combustion engines and which exhibit improved oxidation and wear performance. More particularly, lubricating oil compositions are described which comprise

- 10 (A) a major amount of oil of lubricating viscosity;
 (B) at least about 1.0% by weight of at least one carboxylic derivative composition produced by reacting
 (B-1) at least one substituted succinic acylating agent with
 (B-2) at least one amine compound characterized by the presence within its structure of at least one
 15 HN< group wherein said substituted succinic acylating agents consist of substituent groups and
 succinic groups wherein the substituent groups are derived from polyalkene, said polyalkene being
 characterized by an Mn value of 1300 to about 5000 and an Mw/Mn value of about 1.5 to about 4.5,
 said acylating agents being characterized by the presence within their structure of an average of at
 least 1.3 succinic groups for each equivalent weight of substituent groups; and
 (C) at least one manganese compound in an amount sufficient to provide from 1 to about 500 ppm of
 20 manganese as metal, provided that the manganese compound is not a neutral manganese dihydrocarbyl
 phosphorodithioate, and
 (D) from about 0.01% to about 5% by weight of a mixture of metal salts of dihydrocarbyl-
 phosphorodithioic acids wherein at least one metal dihydrocarbylphosphorodithioate is characterized by
 the general formula

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wherein R¹ and R² are each independently hydrocarbyl groups containing from 3 to about 13 carbon
 35 atoms, M is a metal, and n is an integer equal to the valence of M wherein in at least one of the
 dihydrocarbylphosphorodithioic acids, one of the hydrocarbyl groups (D-1) is an isopropyl or secondary
 butyl group, the other hydrocarbyl group (D-2) contains at least 5 carbon atoms, and at least about 10
 mole percent of all of the hydrocarbyl groups present in (D) are isopropyl groups, secondary butyl
 groups, or mixtures thereof.

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The oil compositions also may contain other desirable additives including

- (E) detergent effective amounts of at least one neutral or basic alkali metal salt of a sulfonic or carboxylic
 acid; and/or
 (F) at least one carboxylic ester derivative as defined herein.

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In one embodiment, the oil compositions of the present invention contain the above additives and other
 additives described in the specification in an amount sufficient to enable the oil to meet all the performance
 requirements of the API Service Classification identified as "SG".

Detailed Description of the Invention

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Throughout this specification and claims, references to percentages by weight of the various compo-
 nents, except for component (A) which is oil, are on a chemical basis unless otherwise indicated. For
 example, when the oil compositions of the invention are described as containing at least 2% by weight of
 (B), the oil composition comprises at least 2% by weight of (B) on a chemical basis. Thus, if component (B)
 is available as a 50% by weight oil solution, at least 4% by weight of the oil solution would be included in
 55 the oil composition.

The number of equivalents of the acylating agent depends on the total number of carboxylic functions
 present. In determining the number of equivalents for the acylating agents, those carboxylic functions which
 are not capable of reacting as a carboxylic acid acylating agent are excluded. In general, however, there is

one equivalent of acylating agent for each carboxy group in these acylating agents. For example, there are two equivalents in an anhydride derived from the reaction of one mole of olefin polymer and one mole of maleic anhydride. Conventional techniques are readily available for determining the number of carboxyl functions (e.g., acid number, saponification number) and, thus, the number of equivalents of the acylating agent can be readily determined by one skilled in the art.

The equivalent weight of an amine or a polyamine is the molecular weight of the amine or polyamine divided by the total number of nitrogens present in the molecule. Thus, ethylene diamine has an equivalent weight equal to one-half of its molecular weight; diethylene triamine has an equivalent weight equal to one-third its molecular weight. The equivalent weight of a commercially available mixture of polyalkylene polyamine can be determined by dividing the atomic weight of nitrogen (14) by the %N contained in the polyamine and multiplying by 100; thus, a polyamine mixture containing 34% nitrogen would have an equivalent weight of 41.2. The equivalent weight of ammonia or a monoamine is the molecular weight.

The equivalent weight of a hydroxyl-substituted amine to be reacted with the acylating agents to form the carboxylic derivative (B) is its molecular weight divided by the total number of nitrogen groups present in the molecule. For the purpose of this invention in preparing component (B), the hydroxyl groups are ignored when calculating equivalent weight. Thus, ethanolamine would have an equivalent weight equal to its molecular weight, and diethanolamine has an equivalent weight (based on nitrogen) equal to its molecular weight.

The equivalent weight of a hydroxyl-substituted amine used to form the carboxylic ester derivatives (F) useful in this invention is its molecular weight divided by the number of hydroxyl groups present, and the nitrogen atoms present are ignored. Thus, when preparing esters from, e.g., diethanolamine, the equivalent weight is one-half the molecular weight of diethanolamine.

The terms "substituent", "acylating agent" and "substituted succinic acylating agent" are to be given their normal meanings. For example, a substituent is an atom or group of atoms that has replaced another atom or group in a molecule as a result of a reaction. The terms acylating agent or substituted succinic acylating agent refer to the compound per se and does not include unreacted reactants used to form the acylating agent or substituted succinic acylating agent.

(A) Oil of Lubricating Viscosity.

The oil which is utilized in the preparation of the lubricants of the invention may be based on natural oils, synthetic oils, or mixtures thereof.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, etc.); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

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

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the

2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

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

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricating oil (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methylhexyl)silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxo)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, etc.). Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans and the like.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the concentrates of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, hydrotreating, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed, recycled or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

(B) Carboxylic Derivatives.

Component (B) which is utilized in the lubricating oils of the present invention is at least one carboxylic derivative composition produced by reacting (B-1) at least one substituted succinic acylating agent with (B-2) at least one amine compound containing at least one HN< group, and wherein said acylating agent consists of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene characterized by an Mn value of about 1300 to about 5000 and an Mu/Mn ratio of about 1.5 to about 4.5, said acylating agents being characterized by the presence within their structure of an average of at least about 1.3 succinic groups for each equivalent weight of substituent groups. Generally, the reaction involves from about 0.5 equivalent to about 2 moles of the amine compound per equivalent of acylating agent.

The carboxylic derivatives (B) are included in the oil compositions to improve dispersancy and VI properties of the oil compositions. In general from about 1% to about 10% or 15% by weight of component (B) can be included in the oil compositions, although the oil compositions preferably will contain at least 2% and in some instances 3% or more by weight of component (B).

The substituted succinic acylating agent (B-1) utilized in the preparation of the carboxylic derivative (B) can be characterized by the presence within its structure of two groups or moieties. The first group or moiety is referred to hereinafter, for convenience, as the "substituent group(s)" and is derived from a polyalkene. The polyalkene from which the substituent groups are derived is characterized by an Mn (number average molecular weight) value of from about 1300 to about 5000, and an Mw/Mn value of at least about 1.5 and more generally from about 1.5 to about 4.5 or about 1.5 to about 4.0. The abbreviation Mw is the conventional symbol representing the weight average molecular weight. Gel permeation chromatography (GPC) is a method which provides measurements of molecular sizes from which both weight average and number average molecular weights as well as the entire molecular weight distribution of the polymers may be determined. 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 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.

The second group or moiety in the acylating agent is referred to herein as the "succinic group(s)". The succinic groups are those groups characterized by the general formula



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wherein X and X' are the same or different provided at least one of X and X' is such that the substituted succinic acylating agent can function as carboxylic acylating agents. That is, at least one of X and X' must be such that the substituted acylating agent can form amides or amine salts with amino compounds, and otherwise function as a conventional carboxylic acid acylating agents. Transesterification and transamidation reactions are considered, for purposes of this invention, as conventional acylating reactions.

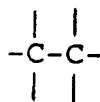
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Thus, X and/or X' is usually -OH, -O-hydrocarbyl, -O-M⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, -Br, and together, X and X' can be -O- so as to form the anhydride. The specific identity of any X or X' group which is not one of the above is not critical so long as its presence does not prevent the remaining group from entering into acylation reactions. Preferably, however, X and X' are each such that both carboxyl functions of the succinic group (i.e., both -C(O)X and -C(O)X' can enter into acylation reactions.

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One of the unsatisfied valences in the grouping

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of general formula I forms a carbon carbon bond with a carbon atom in the substituent group. While other such unsatisfied valence may be satisfied by a similar bond with the same or different substituent group, all but the said one such valence is usually satisfied by hydrogen; i.e., -H.

The substituted succinic acylating agents are characterized by the presence within their structure of an average of at least 1.3 succinic groups (that is, groups corresponding to general formula I) for each equivalent weight of substituent groups. For purposes of this invention, the equivalent weight of substituent groups is deemed to be the number obtained by dividing the Mn value of the polyalkene from which the substituent is derived into the total weight of the substituent groups present in the substituted succinic acylating agents. Thus, if a substituted succinic acylating agent is characterized by a total weight of substituent group of 40,000 and the Mn value for the polyalkene from which the substituent groups are derived is 2000, then that substituted succinic acylating agent is characterized by a total of 20 (40,000/2000 = 20) equivalent weights of substituent groups. Therefore, that particular succinic acylating agent must also be characterized by the presence within its structure of at least 26 succinic groups to meet one of the requirements of the succinic acylating agents used in this invention.

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Another requirement for the substituted succinic acylating agents is that the substituent groups must have been derived from a polyalkene characterized by an Mw/Mn value of at least about 1.5. The upper limit of Mw/Mn will generally be about 4.5. Values of from 1.5 to about 4.5 are particularly useful.

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Polyalkenes having the Mn and Mw values discussed above are known in the art and can be prepared according to conventional procedures. For example, some of these polyalkenes are described and exemplified in U.S. Patent 4,234,435. Several such polyalkenes, especially polybutenes, are commercially available.

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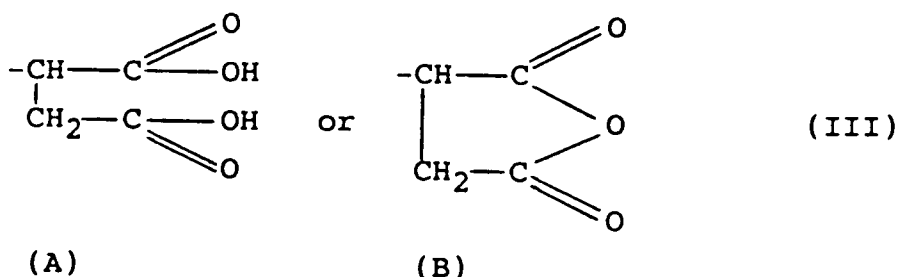
In one preferred embodiment, the succinic groups will normally correspond to the general formula

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wherein R and R' are each independently selected from the group consisting of -OH, -Cl, -O-lower alkyl, and when taken together, R and R' are -O-. In the latter case, the succinic group is a succinic anhydride group. All the succinic groups in a particular succinic acylating agent need not be the same, but they can be the same. Preferably, the succinic groups will correspond to



and mixtures of (III(A)) and (III(B)). Providing substituted succinic acylating agents wherein the succinic groups are the same or different is within the ordinary skill of the art and can be accomplished through conventional procedures such as treating the substituted succinic acylating agents themselves (for example, hydrolyzing the anhydride to the free acid or converting the free acid to an acid chloride with thionyl chloride) and/or selecting the appropriate maleic or fumaric reactants.

As previously mentioned, the minimum number of succinic groups for each equivalent weight of substituent group is 1.3. The maximum number generally will not exceed 4.5. Generally the minimum will be about 1.4 succinic groups for each equivalent weight of substituent group. A range based on this minimum is at least 1.4 to about 3.5, and more specifically about 1.4 to about 2.5 succinic groups per equivalent weight of substituent groups.

In addition to preferred substituted succinic groups where the preference depends on the number and identity of succinic groups for each equivalent weight of substituent groups, still further preferences are based on the identity and characterization of the polyalkenes from which the substituent groups are derived.

With respect to the value of Mn for example, a minimum of about 1300 and a maximum of about 5000 are preferred with an Mn value in the range of from about 1500 to about 5000 also being preferred. A more preferred Mn value is one in the range of from about 1500 to about 2800. A most preferred range of Mn values is from about 1500 to about 2400.

Before proceeding to a further discussion of the polyalkenes from which the substituent groups are derived, it should be pointed out that these preferred characteristics of the succinic acylating agents are intended to be understood as being both independent and dependent. They are intended to be independent in the sense that, for example, a preference for a minimum of 1.4 or 1.5 succinic groups per equivalent weight of substituent groups is not tied to a more preferred value of Mn or Mw/Mn. They are intended to be dependent in the sense that, for example, when a preference for a minimum of 1.4 or 1.5 succinic groups is combined with more preferred values of Mn and/or Mw/Mn, the combination of preferences does in fact describe still further more preferred embodiments of the invention. Thus, the various parameters are intended to stand alone with respect to the particular parameter being discussed but can also be combined with other parameters to identify further preferences. This same concept is intended to apply throughout the specification with respect to the description of preferred values, ranges, ratios, reactants, and the like unless a contrary intent is clearly demonstrated or apparent.

In one embodiment, when the Mn of a polyalkene is at the lower end of the range, e.g., about 1300, the ratio of succinic groups to substituent groups derived from said polyalkene in the acylating agent is preferably higher than the ratio when the Mn is, for example, 1500. Conversely when the Mn of the polyalkene is higher, e.g., 2000, the ratio may be lower than when the Mn of the polyalkene is, e.g., 1500.

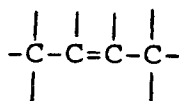
The polyalkenes from which the substituent groups are derived are homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms; usually 2 to about 6 carbon atoms. The interpolymers are those in which two or more olefin monomers are interpolymerized according to well-known conventional procedures to form polyalkenes having units within their structure derived from each of said two or more olefin monomers. Thus, "interpolymer(s)" as used herein is inclusive of copolymers, terpolymers, tetrapolymers, and the like. As will be apparent to those of ordinary skill in the art, the polyalkenes from which the substituent groups are derived are often conventionally referred to as "polyolefin(s)".

The olefin monomers from which the polyalkenes are derived are polymerizable olefin monomers characterized by the presence of one or more ethylenically unsaturated groups (i.e., $>C=C<$); that is, they are monoolefinic monomers such as ethylene, propylene, butene-1, isobutene, and octene-1 or polyolefinic monomers (usually diolefinic monomers) such as butadiene-1,3 and isoprene.

These olefin monomers are usually polymerizable terminal olefins; that is, olefins characterized by the presence in their structure of the group $>C=CH_2$. However, polymerizable internal olefin monomers

(sometimes referred to in the literature as medial olefins) characterized by the presence within their structure of the group

5



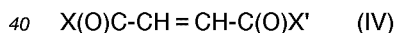
10 can also be used to form the polyalkenes. When internal olefin monomers are employed, they normally will be employed with terminal olefins to produce polyalkenes which are interpolymers. For purposes of this invention, when a particular polymerized olefin monomer can be classified as both a terminal olefin and an internal olefin, it will be deemed to be a terminal olefin. Thus, 1,3-pentadiene (i.e., piperylene) is deemed to be a terminal olefin for purposes of this invention.

15 Some of the substituted succinic acylating agents (B-1) useful in preparing the carboxylic esters (B) are known in the art and are described in, for example, U.S. Patent 4,234,435. The acylating agents described in the '435 patent are characterized as containing substituent groups derived from polyalkenes having an Mn value of about 1300 to about 5000, and an Mw/Mn value of about 1.5 to about 4.

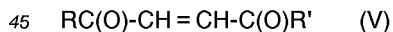
20 There is a general preference for aliphatic, hydrocarbon polyalkenes free from aromatic and cycloaliphatic groups. Within this general preference, there is a further preference for polyalkenes which are derived from the group consisting of homopolymers and interpolymers of terminal hydrocarbon olefins of 2 to about 16 carbon atoms. This further preference is qualified by the proviso that, while interpolymers of terminal olefins are usually preferred, interpolymers optionally containing up to about 40% of polymer units derived from internal olefins of up to about 16 carbon atoms are also within a preferred group. A more
25 preferred class of polyalkenes are those selected from the group consisting of homopolymers and interpolymers of terminal olefins of 2 to about 6 carbon atoms, more preferably 2 to 4 carbon atoms. However, another preferred class of polyalkenes are the latter more preferred polyalkenes optionally containing up to about 25% of polymer units derived from internal olefins of up to about 6 carbon atoms.

Obviously, preparing polyalkenes as described above which meet the various criteria for Mn and
30 Mw/Mn is within the skill of the art and does not comprise part of the present invention. Techniques readily apparent to those skilled in the art include controlling polymerization temperatures, regulating the amount and type of polymerization initiator and/or catalyst, employing chain terminating groups in the polymerization procedure, and the like. Other conventional techniques such as stripping (including vacuum stripping) a very light end and/or oxidatively or mechanically degrading high molecular weight polyalkene to produce
35 lower molecular weight polyalkenes can also be used.

In preparing the substituted succinic acylating agents of this invention, one or more of the above-described polyalkenes is reacted with one or more acidic reactants selected from the group consisting of maleic or fumaric reactants of the general formula



wherein X and X' are as defined hereinbefore in Formula I. Preferably the maleic and fumaric reactants will be one or more compounds corresponding to the general formula



wherein R and R' are as previously defined in Formula II herein. Ordinarily, the maleic or fumaric reactants will be maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. The maleic reactants are usually preferred over the fumaric reactants because the former are more readily available
50 and are, in general, more readily reacted with the polyalkenes (or derivatives thereof) to prepare the substituted succinic acylating agents of the present invention. The especially preferred reactants are maleic acid, maleic anhydride, and mixtures of these. Due to availability and ease of reaction, maleic anhydride will usually be employed.

Examples of patents describing various procedures for preparing useful acylating agents include U.S.
55 Patents 3,215,707 (Rense); 3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219.

For convenience and brevity, the term "maleic reactant" is often used hereinafter. When used, it should be understood that the term is generic to acidic reactants selected from maleic and fumaric reactants

corresponding to Formulae (IV) and (V) above including a mixture of such reactants.

The acylating reagents described above are intermediates in processes for preparing the carboxylic derivative compositions (B) comprising reacting (B-1) one or more acylating reagents with (B-2) at least one amino compound characterized by the presence within its structure of at least one HN< group.

The amino compound (B-2) characterized by the presence within its structure of at least one HN< group can be a monoamine or polyamine compound. Mixtures of two or more amino compounds can be used in the reaction with one or more acylating reagents of this invention. Preferably, the amino compound contains at least one primary amino group (i.e., -NH₂) and more preferably the amine is a polyamine, especially a polyamine containing at least two -NH- groups, either or both of which are primary or secondary amines. The amines may be aliphatic, cycloaliphatic, aromatic or heterocyclic amines. The polyamines not only result in carboxylic acid derivative compositions which are usually more effective as dispersant/detergent additives, relative to derivative compositions derived from monoamines, but these preferred polyamines result in carboxylic derivative compositions which exhibit more pronounced V.I. improving properties.

Among the preferred amines are the alkylene polyamines, including the polyalkylene polyamines. The alkylene polyamines include those conforming to the general formula



wherein n is from 1 to about 10; each R³ is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted or amine-substituted hydrocarbyl group having up to about 30 atoms, or two R³ groups on different nitrogen atoms can be joined together to form a U group, with the proviso that at least one R³ group is a hydrogen atom and U is an alkylene group of about 2 to about 10 carbon atoms. Preferably U is ethylene or propylene. Especially preferred are the alkylene polyamines where each R³ is hydrogen or an amino-substituted hydrocarbyl group with the ethylene polyamines and mixtures of ethylene polyamines being the most preferred. Usually n will have an average value of from about 2 to about 7. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related amino alkyl-substituted piperazines are also included.

Alkylene polyamines useful in preparing the carboxylic derivative compositions (B) include ethylene diamine, triethylene tetramine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di-(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, N-(2-aminoethyl)piperazine, 1,4-bis(2-aminoethyl)piperazine, and the like. Higher homologs as are obtained by condensing two or more of the above-illustrated alkylene amines are useful, as are mixtures of two or more of any of the afore-described polyamines.

Ethylene polyamines, such as those mentioned above, are especially useful for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in The Encyclopedia of Chemical Technology, Second Edition, Kirk and Othmer, Volume 7, pages 27-39, Interscience Publishers, Division of John Wiley and Sons, 1965. Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia, etc. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines. The mixtures are particularly useful in preparing carboxylic derivative (B) useful in this invention. On the other hand, quite satisfactory products can also be obtained by the use of pure alkylene polyamines.

Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures. In this instance, lower molecular weight polyamines and volatile contaminants are removed from an alkylene polyamine mixture to leave as residue what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than two, usually less than 1% (by weight) material boiling below about 200°C. In the instance of ethylene polyamine bottoms, which are readily available and found to be quite useful, the bottoms contain less than about 2% (by weight) total diethylene triamine (DETA) or triethylene tetramine (TETA). A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" showed 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 showed it to contain about 0.93% "Light Ends" (most probably DETA), 0.72% TETA, 21.74% tetraethylene pentamine and 76.61% pentaethylene hexamine and higher (by weight). These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like.

Other polyamines which can be reacted with the acylating agents (B-1) in accordance with this invention to form the carboxylic derivatives (B) of this invention are described in, for example, U.S. Patents 3,219,666 and 4,234,435.

The carboxylic derivative compositions (B) produced from the acylating reagents (B-1) and the amino compounds (B-2) described hereinbefore comprise acylated amines which include amine salts, amides, imides and imidazolines as well as mixtures thereof. To prepare the carboxylic acid derivatives from the acylating reagents and the amino compounds, one or more acylating reagents and one or more amino compounds are heated, optionally in the presence of a normally liquid, substantially inert organic solvent/diluent, at temperatures in the range of about 80 °C up to the decomposition point (where the decomposition point is as previously defined) but normally at temperatures in the range of about 100 °C up to about 300 °C provided 300 °C does not exceed the decomposition point. Temperatures of about 125 °C to about 250 °C are normally used. The acylating reagent and the amino compound are reacted in amounts sufficient to provide from about one-half equivalent up to about 2 moles of amino compound per equivalent of acylating reagent.

Because the acylating reagents (B-1) can be reacted with the amine compounds (B-2) in the same manner as the high molecular weight acylating agents of the prior art are reacted with amines, U.S. Patents 3,172,892, 3,219,666; 3,272,746; and 4,234,435 are expressly cited for their disclosures with respect to the procedures applicable to reacting the acylating reagents with the amino compounds as described above.

In order to produce carboxylic derivative compositions exhibiting viscosity improving capabilities, it has been found generally necessary to react the acylating reagents with polyfunctional amine reactants. For example, polyamines having two or more primary and/or secondary amino groups are preferred. Obviously, however, it is not necessary that all of the amino compounds reacted with the acylating reagents be polyfunctional. Thus, combinations of mono and polyfunctional amino compounds be used.

In one embodiment, the acylating agent is reacted with from about 0.70 equivalent to less than 1 equivalent (e.g., about 0.95 equivalent) of amino compound, per equivalent of acylating agent. The lower limit on the equivalents of amino compound may be 0.75 or even 0.80 up to about 0.90 or 0.95 equivalent, per equivalent of acylating agent. Thus narrower ranges of equivalents of acylating agents (B-1) to amino compounds (B-2) may be from about 0.70 to about 0.90 or about 0.75 to about 0.90 or about 0.75 to about 0.85. It appears, at least in some situations, that when the equivalent of amino compound is about 0.75 or less, per equivalent of acylating agent, the effectiveness of the carboxylic derivatives as dispersants is reduced. In one embodiment, the relative amounts of acylating agent and amine are such that the carboxylic derivative preferably contains no free carboxyl groups.

In another embodiment, the acylating agent is reacted with from about 1.0 to about 1.1 or up to about 1.5 equivalents of amino compound, per equivalent of acylating agent. Increasing amounts of the amino compound also can be used.

The amount of amine compound (B-2) within the above ranges that is reacted with the acylating agent (B-1) may also depend in part on the number and type of nitrogen atoms present. For example, a smaller amount of a polyamine containing one or more -NH₂ groups is required to react with a given acylating agent than a polyamine having the same number of nitrogen atoms and fewer or no -NH₂ groups. One -NH₂ group can react with two -COOH groups to form an imide. If only secondary nitrogens are present in the amine compound, each >NH group can react with only one -COOH group. Accordingly, the amount of polyamine within the above ranges to be reacted with the acylating agent to form the carboxylic derivatives of the invention can be readily determined from a consideration of the number and types of nitrogen atoms in the polyamine (i.e., -NH₂, >NH, and >N-).

In addition to the relative amounts of acylating agent and amino compound used to form the carboxylic derivative composition (B), other features of the carboxylic derivative compositions used in this invention are the Mn and the Mw/Mn values of the polyalkene as well as the presence within the acylating agents of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups. When all of these features are present in the carboxylic derivative compositions (B), the lubricating oil compositions of the present invention exhibit novel and improved properties, and the lubricating oil compositions are characterized by improved performance in combustion engines.

The ratio of succinic groups to the equivalent weight of substituent group present in the acylating agent can be determined from the saponification number of the reacted mixture corrected to account for

unreacted polyalkene present in the reaction mixture at the end of the reaction (generally referred to as filtrate or residue in the following examples). Saponification number is determined using the ASTM D-94 procedure. The formula for calculating the ratio from the saponification number is as follows:

$$\text{Ratio} = \frac{(\text{Mn})(\text{Sap No.}, \text{corrected})}{112,200 - 98(\text{Sap No.}, \text{corrected})}$$

The corrected saponification number is obtained by dividing the saponification number by the percent of the polyalkene that has reacted. For example, if 10% of the polyalkene did not react and the saponification number of the filtrate or residue is 95, the corrected saponification number is 95 divided by 0.90 or 105.5.

The preparation of the acylating agents is illustrated in the following Examples 1-3 and the preparation of the carboxylic acid derivative compositions (B) is illustrated by the following Examples B-1 to B-16. In the following examples, and elsewhere in the specification and claims, all percentages and parts are by weight, temperatures are in degrees Celsius and pressures are at or near atmospheric unless otherwise clearly indicated.

Acylating Agents:

Example 1

A mixture of 510 parts (0.28 mole) of polyisobutene (Mn = 1845; Mw = 5325) and 59 parts (0.59 mole) of maleic anhydride is heated to 110 °C. This mixture is heated to 190 °C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192 °C an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 °C with nitrogen blowing for 10 hours. The residue is the desired polyisobutene-substituted succinic acylating agent having a saponification equivalent number of 87 as determined by ASTM procedure D-94.

Example 2

A mixture of 1000 parts (0.495 mole) of polyisobutene (Mn = 2020; Mw = 6049) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 °C. This mixture is heated to 184 °C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 °C an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 °C with nitrogen blowing for 26 hours. The residue is the desired polyisobutene-substituted succinic acylating agent having a saponification equivalent number of 87 as determined by ASTM procedure D-94.

Example 3

A mixture of polyisobutene chloride, prepared by the addition of 251 parts of gaseous chlorine to 3000 parts of polyisobutene (Mn = 1696; Mw = 6594) at 80 °C in 4.66 hours, and 345 parts of maleic anhydride is heated to 200 °C in 0.5 hour. The reaction mixture is held at 200-224 °C for 6.33 hours, stripped at 210 °C under vacuum and filtered. The filtrate is the desired polyisobutene-substituted succinic acylating agent having a saponification equivalent number of 94 as determined by ASTM procedure D-94.

Carboxylic Derivative Compositions (B):

Example B-1

A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having from about 3 to about 10 nitrogen atoms per molecule to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared in Example 1 at 138 °C. The reaction mixture is heated to 150 °C in 2 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the product as an oil solution.

Example B-2

A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having from about 3 to 10 nitrogen atoms per molecule to 1067 parts of mineral oil and 893 parts (1.38 equivalents) of the substituted succinic acylating agent prepared in Example 2 at 140-145 °C. The reaction mixture is heated to 155 °C in 3 hours and stripped by blowing with nitrogen. The reaction mixture is filtered, and the filtrate is the desired product.

Example B-3

A mixture of 1132 parts of mineral oil and 709 parts (1.2 equivalents) of a substituted succinic acylating agent prepared as in Example 1 is prepared, and a solution of 56.8 parts of piperazine (1.32 equivalents) in 200 parts of water is added slowly from a dropping funnel to the above mixture at 130-140 °C over approximately 4 hours. Heating is continued to 160 °C as water is removed. The mixture is maintained at 160-165 °C for one hour and cooled overnight. After reheating the mixture to 160 °C, the mixture is maintained at this temperature for 4 hours. Mineral oil (270 parts) is added, and the mixture is filtered at 150 °C through a filter aid. The filtrate is the desired product containing 65% oil and 0.65% nitrogen (theory, 0.86%).

Example B-4

A mixture of 1968 parts of mineral oil and 1508 parts (2.5 equivalents) of a substituted succinic acylating agent prepared as in Example 1 is heated to 145 °C whereupon 125.6 parts (3.0 equivalents) of a commercial mixture of ethylene polyamines as used in Example B-1 are added over a period of 2 hours while maintaining the reaction temperature at 145-150 °C. The reaction mixture is stirred for 5.5 hours at 150-152 °C while blowing with nitrogen. The mixture is filtered at 150 °C with a filter aid. The filtrate is the desired product containing 55% oil and 1.20% nitrogen (theory, 1.17).

Example B-5

A mixture of 1503 parts of mineral oil and 1220 parts (2 equivalents) of a substituted succinic acylating agent prepared as in Example 1 is heated to 110 °C whereupon 120 parts (3 equivalents) of a commercial mixture of ethylene polyamines of the type used in Example B-1 are added over a period of about 50 minutes. The reaction mixture is stirred an additional 30 minutes at 110 °C, and the temperature is then raised to and maintained at about 151 °C for 4 hours. A filter aid is added and the mixture is filtered. The filtrate is the desired product containing 53.2% oil and 1.44% nitrogen (theory, 1.49).

Example B-6

A mixture of 3111 parts of mineral oil and 844 parts (21 equivalents) of a commercial mixture of ethylene polyamines as used in Example B-1 is heated to 140 °C whereupon 3885 parts (7.0 equivalents) of a substituted succinic acylating agent prepared as in Example 1 are added over a period of about 1.75 hours as the temperature increases to about 150 °C. While blowing with nitrogen, the mixture is maintained at 150-155 °C for a period of about 6 hours and thereafter filtered with a filter aid at 130 °C. The filtrate is the desired product containing 40% oil and 3.5% nitrogen (theory, 3.78).

Example B-7

A mixture is prepared by the addition of 18.2 parts (0.433 equivalent) of a commercial mixture of ethylene polyamines having from about 3 to about 10 nitrogen atoms per molecule to 392 parts of mineral oil and 348 parts (0.52 equivalent) of the substituted succinic acylating agent prepared in Example 2 at 140 °C. The reaction mixture is heated to 150 °C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate which is the desired product containing 55% oil.

Example B-8

An appropriate size flask fitted with a stirrer, nitrogen inlet tube, addition funnel and Dean-Stark trap/condenser is charged with a mixture of 2483 parts acylating agent (4.2 equivalents) as described in

Example 3, and 1104 parts oil. This mixture is heated to 210 °C while nitrogen was slowly bubbled through the mixture. Ethylene polyamine bottoms (134 parts, 3.14 equivalents) are slowly added over about one hour at this temperature. The temperature is maintained at about 210 °C for 3 hours and then 3688 parts oil is added to decrease the temperature to 125 °C. After storage at 138 °C for 17.5 hours, the mixture is
5 filtered through diatomaceous earth to provide the desired acylated amine bottoms containing 65% oil.

Example B-9

A mixture of 3660 parts (6 equivalents) of a substituted succinic acylating agent prepared as in Example
10 1 in 4664 parts of diluent oil is prepared and heated at about 110 °C whereupon nitrogen is blown through the mixture. To this mixture there are then added 210 parts (5.25 equivalents) of a commercial mixture of ethylene polyamines containing from about 3 to about 10 nitrogen atoms per molecule over a period of one hour and the mixture is maintained at 110 °C for an additional 0.5 hour. After heating for 6 hours at 155 °C while removing water, a filter aid is added and the reaction mixture is filtered at about 150 °C. The filtrate is
15 the desired product.

Example B-10

The general procedure of Example B-9 is repeated with the exception that 0.8 equivalent of a
20 substituted succinic acylating agent as prepared in Example 1 is reacted with 0.67 equivalent of the commercial mixture of ethylene polyamines. The product obtained in this manner is an oil solution containing 55% diluent oil.

Example B-11

25 The general procedure of Example B-9 is repeated except that the polyamine used in this example is an equivalent amount of an alkylene polyamine mixture comprising 80% of ethylene polyamine bottoms from Union Carbide and 20% of a commercial mixture of ethylene polyamines corresponding in empirical formula to diethylene triamine. This polyamine mixture is characterized as having an equivalent weight of
30 about 43.3.

Example B-12

35 The general procedure of Example B-9 is repeated except that the polyamine utilized in this example comprises a mixture of 80 parts by weight of ethylene polyamine bottoms available from Dow and 20 parts by weight of diethylenetriamine. This mixture of amines has an equivalent weight of about 41.3.

Example B-13

40 A mixture of 444 parts (0.7 equivalent) of a substituted succinic acylating agent prepared as in Example 1 and 563 parts of mineral oil is prepared and heated to 140 °C whereupon 22.2 parts of an ethylene polyamine mixture corresponding in empirical formula to triethylene tetramine (0.58 equivalent) are added over a period of one hour as the temperature is maintained at 140 °C. The mixture is blown with nitrogen as it is heated to 150 °C and maintained at this temperature for 4 hours while removing water. The mixture
45 then is filtered through a filter aid at about 135 °C, and the filtrate is the desired product comprising about 55% of mineral oil.

Example B-14

50 A mixture of 422 parts (0.7 equivalent) of a substituted succinic acylating agent prepared as in Example 1 and 188 parts of mineral oil is prepared and heated to 210 °C whereupon 22.1 parts (0.53 equivalent) of a commercial mixture of ethylene polyamine bottoms from Dow (E-100) are added over a period of one hour blowing with nitrogen. The temperature of the mixture is then increased to about 210-216 °C and maintained at this temperature for 3 hours. Mineral oil (625 parts) is added and the mixture is maintained at 135 °C for
55 about 17 hours whereupon the mixture is filtered and the filtrate is the desired product containing 65% oil.

Example B-15

A mixture of 414 parts (0.71 equivalent) of a substituted succinic acylating agent prepared as in Example 1 and 184 parts of mineral oil is prepared and heated to about 80 °C whereupon 22.4 parts (0.534 equivalent) of melamine are added. The mixture is heated to 160 °C over a period of about 2 hours and maintained at this temperature for 5 hours. After cooling overnight, the mixture is heated to 170 °C over 2.5 hours and to 215 °C over a period of 1.5 hours. The mixture is maintained at about 215 °C for about 4 hours and at about 220 °C for 6 hours. After cooling overnight, the reaction mixture is filtered at 150 °C through a filter aid. The filtrate is the desired product containing 30% mineral oil.

Example B-16

A mixture of 414 parts (0.71 equivalent) of a substituted acylating agent prepared as in Example 1 and 184 parts of mineral oil is heated to 210 °C whereupon 21 parts (0.53 equivalent) of a commercial mixture of ethylene polyamine corresponding in empirical formula to tetraethylene pentamine are added over a period of 0.5 hour as the temperature is maintained at about 210-217 °C. Upon completion of the addition of the polyamine, the mixture is maintained at 217 °C for 3 hours while blowing with nitrogen. Mineral oil is added (613 parts) and the mixture is maintained at about 135 °C for 17 hours and filtered. The filtrate is the desired product containing 65% mineral oil.

(C) Manganese Compound.

The lubricating oil compositions of the present invention contain at least one manganese compound in an amount which is sufficient to provide from 1 to about 500 ppm of manganese as metal, provided that the manganese compound is not a neutral manganese dihydrocarbyl phosphorodithioate. In one embodiment, the manganese compounds are soluble in the lubricating oil compositions of the invention. The manganese compounds (C) generally are salts of acidic materials, and in particular, salts of carboxylic acids, sulfonic acids, and phenols. In another embodiment, the amount of manganese compound in the oil will provide from about 50 to about 300 ppm of manganese as metal. The manganese compounds may be neutral manganese compounds or "overbased" manganese compounds, and the overbased manganese compounds generally are preferred. The term "overbased" as applied to the manganese compounds utilized in the present invention is an indication that the compounds contain more manganese than is required to neutralize the acid. Thus, overbased manganese salts contain more than one equivalent of metal per equivalent of acid. Overbased manganese salts of acidic materials such as carboxylic acids, sulfonic acids, phenols and phosphorus acids are known and have been described in the art. See, for example, U.S. Patent 4,162,986 (Alkatis); U.S. Patent 3,827,979 (Piotrowski et al); U.S. Patent 3,312,618 (LeSuer et al); U.S. Patents 2,616,904 and '905 (Aseff et al); and U.S. Patent 4,252,659 (Ali). It should be noted that although neutral manganese dihydrocarbyl phosphorodithioates are not included in the lubricating oil compositions of the present invention, overbased manganese dihydrocarbyl phosphorodithioates are contemplated as being useful manganese compounds.

The overbased manganese salts are preferred because they provide high manganese content with retention of solubility and are useful, therefore, for introducing high amounts of metal while minimizing the amount of acidic compound introduced into the lubricating oil which merely serves as a carrier for the manganese metal. As noted, the metal-to-acid mole ratios of overbased manganese compounds is greater than 1 to 1 and is generally greater than 2 to 1. The mole ratio of metal-to-acid in overbased compounds often is referred to as the Metal Ratio.

The organic acids used in the preparation of the manganese salts include carboxylic acids, particularly those containing from 1 to about 30 carbon atoms, sulfonic acids, particularly those containing an aromatic ring structure substituted with one or more alkyl groups of from 4 to about 22 carbon atoms, phenolic compounds, particularly hydrocarbon-substituted phenols; and when the manganese compound is an overbased compound, phosphorus compounds containing within their structures, one or more organic groups of from 1 to about 30 or more carbon atoms. All of these acidic materials are well known in the art.

The carboxylic acids can be aliphatic, cycloaliphatic, or aromatic mono- and polycarboxylic acids. Monocarboxylic acids include C₁₋₇ lower acids (acetic, propionic, etc) and higher C₈₊ acids (e.g., octanoic, decanoic, etc.) as well as the well known fatty acids of about 12-30 carbon atoms. The fatty acids are often mixtures or straight and branched chain acids containing, for example, from 5% to about 30% straight chain acids and about 70% to about 95% (mole) branched chain acids. Other commercially available fatty acid mixtures containing much higher proportions of straight chain acids are also useful. Mixtures produced from

dimerization of unsaturated fatty acids can also be used.

Higher carboxylic acids include the well-known dicarboxylic acids made by alkylating maleic anhydride or its derivatives. The products of such reactions are hydrocarbon substituted succinic acids, anhydrides, and the like. Lower molecular weight dicarboxylic acids, such as the polymethylene bridged acids (glutaric, adipic, and the like), can also be used to make the salts of this invention as well as the lower molecular weight substituted succinic acids such as tetrapropenyl succinic acid and its analogs of to about C₃₀ substituted acids.

Higher molecular weight substituted succinic anhydrides, acids, and analogs described above in the preparation of the dispersants (B) are also useful in making the manganese salts of this invention.

The aliphatic acids generally contain at least 8 carbon atoms and preferably at least 12 carbon atoms. Usually they have no more than about 400 carbon atoms. Generally, if the aliphatic carbon chain is branched, the acids are more oil-soluble for any given carbon atoms content. The cycloaliphatic and aliphatic carboxylic acids can be saturated or unsaturated. Specific examples include 2-ethylhexanoic acid, alpha-linolenic acid, propylene-tetramer-substituted succinic acid, behenic acid, isostearic acid, pelargonic acid, capric acid, palmitoleic acid, linoleic acid, lauric acid, oleic acid, ricinoleic acid, undecylic acid, dioctylcyclopentane carboxylic acid, myristic acid, dilauryldecahydronaphthalene carboxylic acid, stearyl-octahydroindene carboxylic acid, palmitic acid, commercially available mixtures of two or more carboxylic acids such as tall oil acids, rosin acids, and the like.

The manganese salts also can be of oil-soluble organic sulfur acids such as sulfonic, sulfamic, thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acid. Generally they are salts of carboxylic or aliphatic sulfonic acids.

Examples of such carboxylic or aliphatic sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fraction having a Saybolt Viscosity from about 100 seconds at 100 ° F (37.8 ° C) to about 200 seconds at 210 ° F (98.9 ° C); petrolatum sulfonic acids; mono- and polywax substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, diphenyl amine, thiophene, alpha-chloronaphthalene, etc.; other substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbon atoms), cetylphenyl mono-sulfide sulfonic acids, dicetyl thianthrene disulfonic acids, dilauryl beta-naphthyl sulfonic acids, dicapryl nitronaphthalene sulfonic acids and alkaryl sulfonic acids such as dodecylbenzene (bottoms) sulfonic acids. Dodecylbenzene (bottoms) are principally mixtures of mono- and di-dodecylbenzenes.

The aliphatic sulfonic acids include paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, hexapropylene sulfonic acids, tetra-amylene sulfonic acids, polyisobutene sulfonic acids wherein the polyisobutene contains from 20 to 7000 or more carbon atoms, chloro-substituted paraffin wax sulfonic acids, nitro-paraffin wax sulfonic acids, etc.; cycloaliphatic sulfonic acids such as petroleum naphthene sulfonic acids, cetyl cyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, bis-(di-isobutyl) cyclohexyl sulfonic acids, mono- or poly-wax-substituted cyclohexyl sulfonic acids, etc.

Further details concerning sulfonic acids used herein can be found in U.S. Patents 2,616,905; 3,027,325; 3,312,618; 3,350,308; 3,471,403; 3,488,284; 3,595,790; 3,798,012; 3,829,381; 4,100,083; and 4,326,972.

Neutral and overbased manganese salts of phenolic compounds (phenates) also are useful in the lubricants of this invention. Hydrocarbon-substituted phenols, sulfurized phenols and alkylene (e.g., methylene) coupled phenols also are useful. Mixtures of phenols can be used to prepare the manganese salts, or mixtures of separately prepared manganese phenates can be included in the lubricating oils of this invention.

Typically, the organic acids used to make the manganese salts used in this invention are carboxylic acids, sulfonic acids, or mixtures thereof. A particularly useful group of manganese salts are those described in U.S. Patent 4,162,986 to Alkaitis et al discloses manganese compositions and, particularly, of manganese salts of organic acids which are useful in the composition of the present invention.

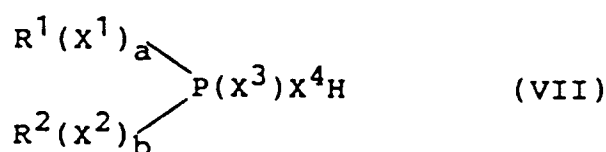
It should be noted that the manganese salts used in this invention are preferably overbased. Such salts are known to the art. See, for example, the just cited U.S. Patent 4,162,986 as well as the following U.S. Patents 3,827,979; 4,252,659; 4,505,718; and 4,664,677. These patents are cited for their disclosure of overbased manganese salts of organic acids.

Particularly useful overbased manganese salts of organic acids are highly overbased manganese metal organic compositions comprising manganese oxide-hydroxide-carboxylate complexes wherein the metal content is in chemical combination partly with oxygen in a polynuclear metal oxide crystallite core and partly with at least two different monocarboxylic acids or a mixture of one or more monocarboxylic and monosulfonic acids containing at least 2 carbon atoms as hydroxyl-metal-carboxylate and hydroxyl-metal-

sulfonate groups, at least one of the acids being a monocarboxylic acid containing at least 7 carbon atoms, and when the second acid is also a monocarboxylic acid, the second acid contains a number of carbon atoms in its longest chain differing by at least 2 carbon atoms from the total number of carbon atoms in the other, at least a portion of the carboxylate and sulfonate groups being hydrogen bonded to oxygen atoms of the core, and the remainder of the carboxylate and sulfonate groups are unbonded and in equilibrium with the bonded groups, and the ratio of total metal moles to the total moles of organic acid is greater than one. These preferred compositions and their method of preparation are described in more detail in U.S. Patent 4,162,986, and in particular, in Cols. 8-14, cited for its disclosure regarding such manganese salts.

Useful overbased manganese salts containing high concentrations of manganese are commercially available from Mooney Chemical Company: FOA 910™ liquid carboxylate containing 40% manganese as metal; and 12% Manganese CEM-ALL®.

Overbased manganese salts made from phosphorus acids also are useful in the lubricants of the invention. The phosphorus acids may be represented by the formula



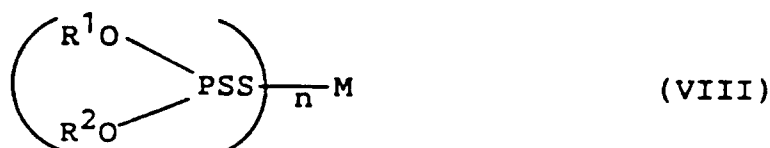
wherein R¹ and R² are each independently hydrocarbon groups;
X¹, X², X³ and X⁴ are each independently oxygen or sulfur; and
a and b are each zero or 1.

The preparation of overbased manganese salts of such phosphorus acids is described in the prior art such as U.S. Patent 2,695,910 (Asseff et al).

In addition to the above-described and required carboxylic derivative dispersants (B) and manganese compounds (C), the lubricants contain other additives to provide additional desirable properties to the oil which are required for acceptable performance in gasoline and diesel engines. Such additives include anti-wear additives such as metal phosphorodithioates (D). Detergents and other dispersants including carboxylic ester derivatives, etc. may also be contained in the lubricants.

(D) Metal Dihydrocarbyl Phosphorodithioates.

In another embodiment, the oil compositions of the present invention also contain (D) at least one metal dihydrocarbyl phosphorodithioate characterized by the general formula



wherein R¹ and R² are each independently hydrocarbyl groups containing from 3 to about 13 carbon atoms, M is a metal, and n is an integer equal to the valence of M.

Generally, the oil compositions of the present invention will contain varying amounts of one or more of the above-identified metal phosphorodithioates such as from about 0.01% to about 5% or from about 0.01% to about 2% by weight, and more generally from about 0.01 to about 1% by weight based on the weight of the total oil composition. The metal phosphorodithioates are added to the lubricating oil compositions of the invention to improve the anti-wear and antioxidant properties of the oil compositions.

The hydrocarbyl groups R¹ and R² in the phosphorodithioate of Formula VIII may be alkyl, cycloalkyl, aralkyl or alkaryl groups, or a substantially hydrocarbon group of similar structure. By "substantially hydrocarbon" is meant hydrocarbons which contain substituent groups such as ether, ester, nitro, or halogen which do not materially affect the hydrocarbon character of the group.

Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl groups, n-hexyl, methylisobutyl, carbinyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative lower alkylphenyl groups include xylyl, cresyl, butylphenyl, amylphenyl, heptylphenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Many substituted hydrocarbon groups may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

The phosphorodithioic acids from which the metal salts useful in this invention are prepared are well known. Examples of dihydrocarbyl phosphorodithioic acids and metal salts, and processes for preparing such acids and salts are found in, for example, U.S. Patents 4,263,150; 4,289,635; 4,308,154; and 4,417,990.

The phosphorodithioic acids are prepared by the reaction of phosphorus pentasulfide with an alcohol or phenol or mixtures of alcohols, mixtures of phenols or mixtures of alcohols and phenols. The reaction involves four moles of the alcohol or phenol per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50°C to about 200°C, preferably from about 50°C to about 150°C. Thus the preparation of O,O-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100°C for about two hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the metal salt of this acid may be effected by reaction with metal oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention.

The metal salts of dihydrocarbyl phosphorodithioates which are useful in this invention include those salts containing Group I metals, Group II metals, aluminum, lead, tin, manganese, cobalt, and nickel. The Group II metals, tin, iron, cobalt, lead, manganese, nickel and copper are among the preferred metals. Zinc and copper are especially useful metals. Examples of metal compounds which may be reacted with the acid include lithium oxide, lithium hydroxide, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, silver oxide, magnesium oxide, magnesium hydroxide, calcium oxide, zinc hydroxide, zinc oxide, copper oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, barium oxide, iron carbonate, copper hydroxide, lead hydroxide, tin butylate, cobalt hydroxide, nickel hydroxide, nickel carbonate, etc.

In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

In one preferred embodiment, the alkyl groups R¹ and R² are derived from secondary alcohols such as isopropyl alcohol, secondary butyl alcohol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, etc.

Especially useful metal phosphorodithioates can be prepared from phosphorodithioic acids which in turn are prepared by the reaction of phosphorus pentasulfide with mixtures of alcohols. In addition, the use of such mixtures enables the utilization of lower cost alcohols which in themselves may not yield oil-soluble phosphorodithioic acids. Thus a mixture of isopropyl and hexyl alcohols can be used to produce a very effective, oil-soluble metal phosphorodithioate. For the same reason mixtures of phosphorodithioic acids can be reacted with the metal compounds to form less expensive, oil-soluble salts.

The mixtures of alcohols may be mixtures of different primary alcohols, mixtures of different secondary alcohols or mixtures of primary and secondary alcohols. Examples of useful mixtures include: n-butanol and n-octanol; n-pentanol and 2-ethyl-1-hexanol; isobutanol and n-hexanol; isobutanol and isoamyl alcohol; isopropanol and 4-methyl-2-pentanol; isopropanol and sec-butyl alcohol; isopropanol and isooctyl alcohol; etc. Particularly useful alcohol mixtures are mixtures of secondary alcohols containing at least about 20 mole percent of isopropyl alcohol, and in a preferred embodiment, at least 40 mole percent of isopropyl alcohol.

In another embodiment, the lubricating oil compositions of the invention contain a mixture of metal salts of dihydrocarbyl phosphorodithioic acids wherein in at least one of the dihydrocarbyl phosphorodithioic acids, one of the hydrocarbyl groups (D-1) is an isopropyl or secondary butyl group, the other hydrocarbyl group (D-2) contains at least five carbon atoms, and at least about 20 mole percent of all of the hydrocarbyl groups present in (D) are isopropyl groups, secondary butyl groups or mixtures thereof.

In yet another embodiment, the lubricating oil compositions contain a mixture of metal salts of dihydrocarbyl phosphorodithioic acids wherein in at least one of the phosphorodithioic acids, one of the hydrocarbyl groups (D-1) is an isopropyl or secondary butyl group and the other hydrocarbyl group (D-2) contains at least five carbon atoms, and the lubricating oil composition contains at least about 0.05 weight percent of isopropyl groups, secondary butyl groups, or mixtures thereof derived from (D). In a further embodiment, the lubricating oil compositions of the invention may contain at least about 0.08 weight

percent of isopropyl and/or secondary butyl groups derived from (D).

The amount of isopropyl or secondary butyl groups derived from (D) in the oil or to be added to the oil can be calculated using the following formula:

5

$$\frac{\text{wt \% of iPr or s-butyl groups} \times \text{wt \% of P in oil} \times 2(43^* \text{ or } 57^*)}{31^*} = \frac{\text{mole \% of iPr or s-butyl groups in hydrocarbon mixture of (D)} \times 100}{100}$$

*43 is molecular weight of an isopropyl group.

15 *57 is molecular weight of a secondary butyl group.

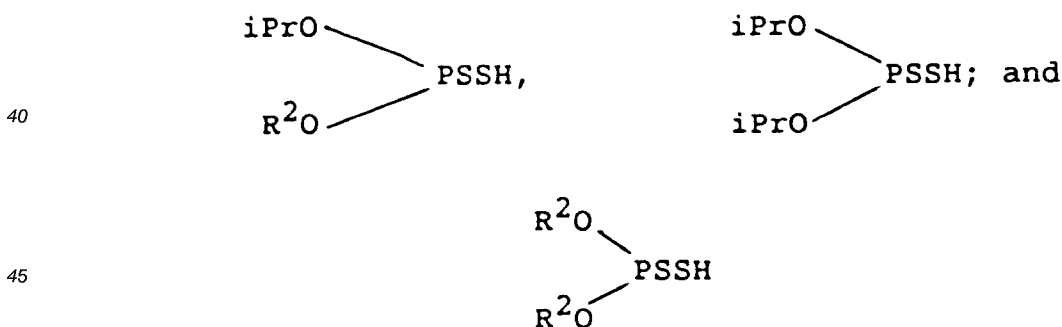
*31 is atomic weight of phosphorous.

The alcohol mixtures which are utilized in the preparation of the phosphorodithioic acids of this last embodiment comprise mixtures of isopropyl alcohol, secondary butyl alcohol or a mixture of isopropyl and secondary butyl alcohols, and at least one primary or aliphatic alcohol containing from about 5 to 13 carbon atoms. In particular, the alcohol mixture will contain at least 20, 25 or 30 mole percent of isopropyl and/or secondary butyl alcohol and will generally comprise from about 20 mole percent to about 90 mole percent of isopropyl or secondary butyl alcohol. In one preferred embodiment, the alcohol mixture will comprise from about 30 to about 70 mole percent of isopropyl alcohol, the remainder being one or more primary aliphatic alcohols.

25 The primary alcohols which may be included in the alcohol mixture include n-amyl alcohol, isoamyl alcohol, n-hexyl alcohol, 2-ethyl-1-hexyl alcohol, isooctyl alcohol, nonyl alcohol, isodecyl alcohol, dodecyl alcohol, tridecyl alcohol, etc. The primary alcohols also may contain various substituent groups such as halogens. Particular examples of useful mixtures of alcohols include, for example, isopropyl/2-ethyl-1-hexyl; isopropyl/isooctyl; isopropyl/isodecyl; isopropyl/dodecyl; and isopropyl/tridecyl. In one preferred embodiment, the primary alcohols will contain from 6 to 13 carbon atoms, and the total number of carbon atoms per phosphorus atom in the required phosphorodithioic acid salt will be at least 9.

30 The composition of the phosphorodithioic acid obtained by the reaction of a mixture of alcohols (e.g., iPrOH and R²OH) with phosphorus pentasulfide is actually a statistical mixture of phosphorodithioic acids as illustrated by the following formulae:

35



45 In the present invention it is preferred to select the amount of the two or more alcohols reacted with P₂S₅ to result in a mixture in which the predominating dithiophosphoric acid is the acid (or acids) containing one isopropyl group or one secondary butyl group, and one primary or secondary alkyl group containing at least 5 carbon atoms. The relative amounts of the three phosphorodithioic acids in the mixture is dependent, in part, on the relative amounts of the alcohols in the mixture, steric effects, etc.

50 The following Examples D-1 to D-6 illustrate the preparation of metal phosphorodithioates prepared from mixtures of alcohols.

55

Example D-1

A phosphorodithioic acid is prepared by reacting a mixture of alcohols comprising 6 moles of 4-methyl-2-pentanol and 4 moles of isopropyl alcohol with phosphorus pentasulfide. The phosphorodithioic acid then is reacted with an oil slurry of zinc oxide. The amount of zinc oxide in the slurry is about 1.08 times the theoretical amount required to completely neutralize the phosphorodithioic acid. The oil solution of the zinc phosphorodithioate obtained in this manner (10% oil) contains 9.5% phosphorus, 20.0% sulfur and 10.5% zinc.

Example D-2

A phosphorodithioic acid is prepared by reacting finely powdered phosphorus pentasulfide with an alcohol mixture containing 11.53 moles (692 parts by weight) of isopropyl alcohol and 7.69 moles (1000 parts by weight) of isooctanol. The phosphorodithioic acid obtained in this manner has an acid number of about 178-186 and contains 10.0% phosphorus and 21.0% sulfur. This phosphorodithioic acid is then reacted with an oil slurry of zinc oxide. The quantity of zinc oxide included in the oil slurry is 1.10 times the theoretical equivalent of the acid number of the phosphorodithioic acid. The oil solution of the zinc salt prepared in this manner contains 12% oil, 8.6% phosphorus, 18.5% sulfur and 9.5% zinc.

Example D-3

A phosphorodithioic acid is prepared by reacting a mixture of 1560 parts (12 moles) of isooctyl alcohol and 180 parts (3 moles) of isopropyl alcohol with 756 parts (3.4 moles) of phosphorus pentasulfide. The reaction is conducted by heating the alcohol mixture to about 55 °C and thereafter adding the phosphorus pentasulfide over a period of 1.5 hours while maintaining the reaction temperature at about 60-75 °C. After all of the phosphorus pentasulfide is added, the mixture is heated and stirred for an additional hour at 70-75 °C, and thereafter filtered through a filter aid.

Zinc oxide (282 parts, 6.87 moles) is charged to a reactor with 278 parts of mineral oil. The above-prepared phosphorodithioic acid (2305 parts, 6.28 moles) is charged to the zinc oxide slurry over a period of 30 minutes with an exothermic reaction to 60 °C. The mixture then is heated to 80 °C and maintained at this temperature for 3 hours. After stripping to 100 °C and 6 mm.Hg (799,9 Pa), the mixture is filtered twice through a filter aid, and the filtrate is the desired oil solution of the zinc salt containing 10% oil, 7.97% zinc (theory 7.40); 7.21% phosphorus (theory 7.06); and 15.64% sulfur (theory 14.57).

Example D-4

Isopropyl alcohol (396 parts, 6.6 moles) and 1287 parts (9.9 moles) of isooctyl alcohol are charged to a reactor and heated with stirring to 59 °C. Phosphorus pentasulfide (833 parts, 3.75 moles) is then added under a nitrogen sweep. The addition of the phosphorus pentasulfide is completed in about 2 hours at a reaction temperature between 59-63 °C. The mixture then is stirred at 45-63 °C for about 1.45 hours and filtered. The filtrate is the desired phosphorodithioic acid.

A reactor is charged with 312 parts (7.7 equivalents) of zinc oxide and 580 parts of mineral oil. While stirring at room temperature, the above-prepared phosphorodithioic acid (2287 parts, 6.97 equivalents) is added over a period of about 1.26 hours with an exotherm to 54 °C. The mixture is heated to 78 °C and maintained at 78-85 °C for 3 hours. The reaction mixture is vacuum stripped to 100 °C at 19 mm.Hg (2533 Pa). The residue is filtered through a filter aid, and the filtrate is an oil solution (19.2% oil) of the desired zinc salt containing 7.86% zinc, 7.76% phosphorus and 14.8% sulfur.

Example D-5

The general procedure of Example D-4 is repeated except that the mole ratio of isopropyl alcohol to isooctyl alcohol is 1:1. The product obtained in this manner is an oil solution (10% oil) of the zinc phosphorodithioate containing 8.96% zinc, 8.49% phosphorus and 18.05% sulfur.

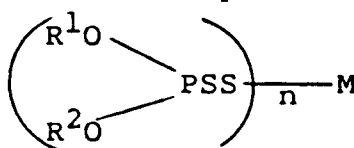
Example D-6

A phosphorodithioic acid is prepared in accordance with the general procedure of Example D-4 utilizing an alcohol mixture containing 520 parts (4 moles) of isooctyl alcohol and 360 parts (6 moles) of isopropyl

alcohol with 504 parts (2.27 moles) of phosphorus pentasulfide. The zinc salt is prepared by reacting an oil slurry of 116.3 parts of mineral oil and 141.5 parts (3.44 moles) of zinc oxide with 950.8 parts (3.20 moles) of the above-prepared phosphorodithioic acid. The product prepared in this manner is an oil solution (10% mineral oil) of the desired zinc salt, and the oil solution contains 9.36% zinc, 8.81% phosphorus and 18.65% sulfur.

Additional specific examples of metal phosphorodithioates useful as component (D) in the lubricating oils of the present invention are listed in the following table. Examples D-7 to D-11 are prepared from single alcohols, and Examples D-12 to D-15 are prepared from alcohol mixtures following the general procedure of Example D-1.

TABLE I
Component D: Metal Phosphorodithioates



<u>Example</u>	<u>R¹</u>	<u>R²</u>	<u>M</u>	<u>n</u>
D-7	n-nonyl	n-nonyl	Ba	2
D-8	cyclohexyl	cyclohexyl	Zn	2
D-9	isobutyl	isobutyl	Zn	2
D-10	hexyl	hexyl	Ca	2
D-11	iso-decyl	iso-decyl	Zn	2
D-12	(n-butyl + dodecyl) (1:1)w		Zn	2
D-13	(isopropyl + isooctyl) (1:1)w		Ba	2
D-14	(isobutyl + isoamyl) (65:35)m		Zn	2
D-15	(isopropyl+sec-butyl) (40:60)m		Zn	2

Another class of the phosphorodithioate additives contemplated for use in the lubricating composition of this invention comprises the adducts of the metal phosphorodithioates described above with an epoxide. The metal phosphorodithioates useful in preparing such adducts are for the most part the zinc phosphorodithioates. The epoxides may be alkylene oxides or arylalkylene oxides. The arylalkylene oxides are exemplified by styrene oxide, p-ethylstyrene oxide, alpha-methylstyrene oxide, 3-beta-naphthyl-1,1,3-butylene oxide, m-dodecylstyrene oxide, and p-chlorostyrene oxide. The alkylene oxides include principally the lower alkylene oxides in which the alkylene radical contains 8 or less carbon atoms. Examples of such lower alkylene oxides are ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, and epichlorohydrin. Other epoxides useful herein include, for example, butyl 9,10-epoxystearate, epoxidized soya bean oil, epoxidized tung oil, and epoxidized styrene-butadiene-copolymer.

The adduct may be obtained by simply mixing the metal phosphorodithioate and the epoxide. The reaction is usually exothermic and may be carried out within wide temperature limits from about 0°C to about 300°C. Because the reaction is exothermic, it is best carried out by adding one reactant, usually the epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexene.

The chemical structure of the adduct is not known. For the purpose of this invention adducts obtained by the reaction of one mole of the phosphorodithioate with from about 0.25 mole to 5 moles, usually up to about 0.75 mole or about 0.5 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, have been found to be especially useful and therefore are preferred.

The preparation of such adducts is more specifically illustrated by the following examples.

Example D-16

A reactor is charged with 2365 parts (3.33 moles) of the zinc phosphorodithioate prepared in Example D-2, and while stirring at room temperature, 38.6 parts (0.67 mole) of propylene oxide are added with an exotherm of from 24-31 °C. The mixture is maintained at 80-90 °C for 3 hours and then vacuum stripped to 101 °C at 7 mm (933.2 Pa). Hg. The residue is filtered using a filter aid, and the filtrate is an oil solution (11.8% oil) of the desired salt containing 17.1% sulfur, 8.17% zinc and 7.44% phosphorus.

Example D-17

To 394 parts (by weight) of zinc dioctylphosphorodithioate having a phosphorus content of 7% there is added at 75-85 °C, 13 parts of propylene oxide (0.5 mole per mole of the zinc phosphorodithioate) throughout a period of 20 minutes. The mixture is heated at 82-85 °C for one hour and filtered. The filtrate (399 parts) is found to contain 6.7% of phosphorus, 7.4% of zinc, and 4.1% of sulfur.

Another class of the phosphorodithioate additives (D) contemplated as useful in the lubricating compositions of the invention comprises mixed metal salts of (a) at least one phosphorodithioic acid of Formula VIII as defined and exemplified above, and (b) at least one aliphatic or alicyclic carboxylic acid. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3 carboxy groups and preferably only 1. It may contain from about 2 to about 40, preferably from about 2 to about 20 carbon atoms, and advantageously about 5 to about 20 carbon atoms. The preferred carboxylic acids are those having the formula R^3COOH , wherein R^3 is an aliphatic or alicyclic hydrocarbon-based radical preferably free from acetylenic unsaturation. 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. For the most part, R^3 is a saturated aliphatic group and especially a branched alkyl group such as the isopropyl or 3-heptyl group. Illustrative polycarboxylic acids are succinic, alkyl- and alkenylsuccinic, adipic, sebacic and citric acids.

The mixed metal salts may be prepared by merely blending a metal salt of a phosphorodithioic acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of phosphorodithioic to carboxylic acid salts is between about 0.5:1 to about 400:1. Preferably, the ratio is between about 0.5:1 and about 200:1. Advantageously, the ratio can be from about 0.5:1 to about 100:1, preferably from about 0.5:1 to about 50:1, and more preferably from about 0.5:1 to about 20:1. Further, the ratio can be from about 0.5:1 to about 4.5:1, preferably about 2.5:1 to about 4.25:1. For this purpose, the equivalent weight of a phosphorodithioic acid is its molecular weight divided by the number of -PSSH groups therein, and that of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the mixed metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio and to react the acid mixture with a suitable metal base. 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, mixed metal salts containing 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.

Variants of the above-described methods may also be used to prepare the mixed metal salts useful in this invention. For example, a metal salt of either acid may be blended with an acid of the other, and the resulting blend reacted with additional metal base.

Suitable metal bases for the preparation of the mixed metal salts include the free metals previously enumerated and their oxides, hydroxides, alkoxides and basic salts. Examples are sodium hydroxide, potassium hydroxide, magnesium oxide, calcium hydroxide, zinc oxide, lead oxide, nickel oxide and the like.

The temperature at which the mixed metal salts are prepared is generally between about 30 °C and about 150 °C, preferably up to about 125 °C. If the mixed salts are prepared by neutralization of a mixture of acids with a metal base, it is preferred to employ temperatures above about 50 °C and especially above about 75 °C. It is frequently advantageous to conduct the reaction in the presence of a substantially inert, normally liquid organic diluent such as naphtha, benzene, xylene, mineral oil or the like. If the diluent is mineral oil or is physically and chemically similar to mineral oil, it frequently need not be removed before using the mixed metal salt as an additive for lubricants or functional fluids.

U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these mixed metal salts and disclose a number of examples of such mixed salts.

The preparation of the mixed salts is illustrated by the following examples.

Example D-18

A mixture of 67 parts (1.63 equivalents) of zinc oxide and 48 parts of mineral oil is stirred at room temperature and a mixture of 401 parts (1 equivalent) of di-(2-ethylhexyl) phosphorodithioic acid and 36 parts (0.25 equivalent) of 2-ethylhexanoic acid is added over 10 minutes. The temperature increases to 40 °C during the addition. When addition is complete, the temperature is increased to 80 °C for 3 hours. The mixture is then vacuum stripped at 100 °C to yield the desired mixed metal salt as a 91% solution in mineral oil.

Example D-19

Following the procedure of Example D-18, a product is prepared from 383 parts (1.2 equivalents) of a dialkyl phosphorodithioic acid containing 65% isobutyl and 35% amyl groups, 43 parts (0.3 equivalent) of 2-ethylhexanoic acid, 71 parts (1.73 equivalents) of zinc oxide and 47 parts of mineral oil. The resulting mixed metal salt, obtained as a 90% solution in mineral oil, contains 11.07% zinc.

(E) Neutral or Basic Alkali Metal Salt.

The lubricating oil compositions of this invention also may contain at least one neutral or basic alkali metal salt of at least one sulfonic or carboxylic acid. The amount of alkali metal salt in the lubricating oil is an amount which is effective to provide the desired detergent properties to the oil. Generally, the lubricants will contain from about 0.01% to about 5% of the alkali metal salt, and more often from about 0.01% to about 3%. A general description of some of the alkali metal salts useful as component (E) is contained in U.S. Patent 4,326,972 (Chamberlin). This patent discloses useful alkali metal salts and methods for preparing said salts.

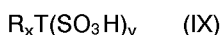
The alkali metals present in the basic alkali metal salts include principally lithium, sodium and potassium, with sodium and potassium being preferred.

The equivalent weight of the acidic organic compound is its molecular weight divided by the number of acidic groups (i.e., sulfonic acid or carboxy groups) present per molecule.

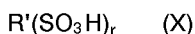
In one preferred embodiment, the alkali metal salts (E) are basic alkali metal salts having metal ratios of at least about 2 and more generally from about 4 to about 40, preferably from about 6 to about 30 and especially from about 8 to about 25.

The acidic organic compound from which the salt of component (E) is derived may be at least one sulfur acid, carboxylic acid, phosphorus acid, or phenol or mixtures thereof. The sulfur acids include the sulfonic acids, thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acids.

The sulfonic acids which are useful in preparing component (E) include those represented by the general formulae



and



In these general formulae, R' is an aliphatic or aliphatic-substituted cycloaliphatic hydrocarbon or essentially hydrocarbon group free from acetylenic unsaturation and containing up to about 60 carbon atoms. When R' is aliphatic, it usually contains at least about 15 carbon atoms; when it is an aliphatic-substituted cycloaliphatic group, the aliphatic substituents usually contain a total of at least about 12 carbon atoms. Examples of R' are alkyl, alkenyl and alkoxyalkyl groups, and aliphatic-substituted cycloaliphatic groups wherein the aliphatic substituents are alkyl, alkenyl, alkoxy, alkoxyalkyl, carboxyalkyl and the like. Generally, the cycloaliphatic nucleus is derived from a cycloalkane or a cycloalkene such as cyclopentane, cyclohexane, cyclohexene or cyclopentene. Specific examples of R' are cetylcyclohexyl, laurylcyclohexyl, cetylox-yethyl, octadecenyl, and groups derived from petroleum, saturated and unsaturated paraffin wax, and olefin polymers including polymerized monoolefins containing about 2-8 carbon atoms per olefinic monomer unit and diolefins containing 4 to 8 carbon atoms per monomer unit. R' can also contain other substituents such as phenyl, cycloalkyl, hydroxy, mercapto, halo, nitro, amino, nitroso, lower alkoxy, lower alkylmercapto, carboxy, carbalkoxy, oxo or thio, or interrupting groups such as -NH-, -O- or -S-, as long as the essentially hydrocarbon character is not destroyed.

R in Formula IX is generally a hydrocarbon or essentially hydrocarbon group free from acetylenic unsaturation and containing from about 4 to about 60 aliphatic carbon atoms, preferably an aliphatic hydrocarbon group such as an alkyl or alkenyl group. It may also, however, contain substituents or interrupting groups such as those enumerated above provided the essentially hydrocarbon character thereof is retained. In general, any non-carbon atoms present in R' or R do not account for more than 10% of the total weight thereof.

T is a cyclic moiety which may be derived from an aromatic hydrocarbon such as benzene, naphthalene, anthracene or biphenyl, or from a heterocyclic compound such as pyridine, indole or isoindole. Ordinarily, T is an aromatic hydrocarbon moiety, especially a benzene or naphthalene group.

The subscript x is at least 1 and is generally 1-3. The subscripts r and y have an average value of about 1-2 per molecule and are generally also 1.

The sulfonic acids are generally petroleum sulfonic acids or synthetically prepared alkaryl sulfonic acids. Among the petroleum sulfonic acids, the most useful products are those prepared by the sulfonation of suitable petroleum fractions with a subsequent removal of acid sludge, and purification. Synthetic alkaryl sulfonic acids are prepared usually from alkylated benzenes such as the Friedel-Crafts reaction products of benzene and polymers such as tetrapropylene. The following are specific examples of sulfonic acids useful in preparing the salts (E). It is to be understood that such examples serve also to illustrate the salts of such sulfonic acids useful as component (E). In other words, for every sulfonic acid enumerated, it is intended that the corresponding basic alkali metal salts thereof are also understood to be illustrated. (The same applies to the lists of other acid materials listed below.) Such sulfonic acids include mahogany sulfonic acids, bright stock sulfonic acids, petrolatum sulfonic acids, mono- and polywax substituted naphthalene sulfonic acids, cetylchlorobenzene sulfonic acids, cetylphenol sulfonic acids, cetylphenol disulfide sulfonic acids, cetoxycapryl benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta-naphthol sulfonic acids, di-capryl nitronaphthalene sulfonic acids, saturated paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, tetraisobutylene sulfonic acids, tetraamylene sulfonic acids, chlorine substituted paraffin wax sulfonic acids, nitroso substituted paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, cetylcyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, mono- and polywax substituted cyclohexyl sulfonic acids, dodecylbenzene sulfonic acids, "dimer alkylate" sulfonic acids, and the like.

Alkyl-substituted benzene sulfonic acids wherein the alkyl group contains at least 8 carbon atoms including dodecyl benzene "bottoms" sulfonic acids are particularly useful. The latter are acids derived from benzene which has been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3, or more branched-chain C₁₂ substituents on the benzene ring. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as by products from the manufacture of household detergents. Similar products obtained from alkylation bottoms formed during manufacture of linear alkyl sulfonates (LAS) are also useful in making the sulfonates used in this invention.

The production of sulfonates from detergent manufacture by-products by reaction with, e.g., SO₃, is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

Other descriptions of basic sulfonate salts which can be incorporated into the lubricating oil compositions of this invention as component (E), and techniques for making them can be found in the following U.S. Patents: 2,174,110; 2,202,781; 2,239,974; 2,319,121; 2,337,552; 3,488,284; 3,595,790; and 3,798,012.

Suitable carboxylic acids from which useful alkaline earth metal salts (E) can be prepared include aliphatic, cycloaliphatic and aromatic mono- and polybasic carboxylic acids including naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids, and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally contain from about 8 to about 50, and preferably from about 12 to about 25 carbon atoms. The cycloaliphatic and aliphatic carboxylic acids are preferred, and they can be saturated or unsaturated. Specific examples include 2-ethylhexanoic acid, linolenic acid, propylene tetramer-substituted maleic acid, behenic acid, isostearic acid, pelargonic acid, capric acid, palmitoleic acid, linoleic acid, lauric acid, oleic acid, ricinoleic acid, undecylic acid, dioctylcyclopentanecarboxylic acid, myristic acid, dilauryldecahydronaphthalene-carboxylic acid, stearyl-octahydroindenecarboxylic acid, palmitic acid, alkyl- and alkenylsuccinic acids, acids formed by oxidation of petrolatum or of hydrocarbon waxes, and commercially available mixtures of two or more carboxylic acids such as tall oil acids, rosin acids, and the like.

In one preferred embodiment, the basic sulfonate salts (E) are oil-soluble dispersions prepared by contacting for a period of time sufficient to form a stable dispersion, at a temperature between the solidification temperature of the reaction mixture and its decomposition temperature:

(E-1) at least one acidic gaseous material selected from the group consisting of carbon dioxide, hydrogen sulfide and sulfur dioxide, with

(E-2) a reaction mixture comprising

(E-2-a) at least one oil-soluble sulfonic acid, or derivative thereof susceptible to overbasing;

5 (E-2-b) at least one alkali metal or basic alkali metal compound;

(E-2-c) at least one lower aliphatic alcohol, alkyl phenol, or sulfurized alkyl phenol; and

(E-2-d) at least one oil-soluble carboxylic acid or functional derivative thereof.

When (E-2-c) is an alkyl phenol or a sulfurized alkyl phenol, component (E-2-d) is optional. A satisfactory basic sulfonic acid salt can be prepared with or without the carboxylic acid in the mixture (E-2).

10 Reagent (E-1) is at least one acidic gaseous material which may be carbon dioxide, hydrogen sulfide or sulfur dioxide; mixtures of these gases are also useful. Carbon dioxide is preferred.

As mentioned above, component (E-2) generally is a mixture containing at least four components of which component (E-2-a) is at least one oil-soluble sulfonic acid as previously defined, or a derivative thereof susceptible to overbasing. Mixtures of sulfonic acids and/or their derivatives may also be used. 15 Sulfonic acid derivatives susceptible to overbasing include their metal salts, especially the alkaline earth, zinc and lead salts; ammonium salts and amine salts (e.g., the ethylamine, butylamine and ethylene polyamine salts); and esters such as the ethyl, butyl and glycerol esters.

Component (E-2-b) is preferably and generally is at least one basic alkali metal compound. Illustrative of basic alkali metal compounds are the hydroxides, alkoxides (typically those in which the alkoxy group 20 contains up to 10 and preferably up to 7 carbon atoms), hydrides and amides. Thus, useful basic alkali metal compounds include sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium propoxide, lithium methoxide, potassium ethoxide, sodium butoxide, lithium hydride, sodium hydride, potassium hydride, lithium amide, sodium amide and potassium amide. Especially preferred are sodium hydroxide and the sodium lower alkoxides (i.e., those containing up to 7 carbon atoms). The equivalent weight of 25 component (E-2-b) for the purpose of this invention is equal to its molecular weight, since the alkali metals are monovalent.

Component (E-2-c) may be at least one lower aliphatic alcohol, preferably a monohydric or dihydric alcohol. Illustrative alcohols are methanol, ethanol, 1-propanol, 1-hexanol, isopropanol, isobutanol, 2- 30 pentanol, 2,2-dimethyl-1-propanol, ethylene glycol, 1,3-propanediol and 1,5-pentanediol. The alcohol also may be a glycol ether such as Methyl Cellosolve. Of these, the preferred alcohols are methanol, ethanol and propanol, with methanol being especially preferred.

Component (E-2-c) also may be at least one alkyl phenol or sulfurized alkyl phenol. The sulfurized alkyl phenols are preferred, especially when (E-2-b) is potassium or one of its basic compounds such as potassium hydroxide. As used herein, the term "phenol" includes compounds having more than one 35 hydroxy group bound to an aromatic ring, and the aromatic ring may be a phenyl or naphthyl ring. The term "alkyl phenol" includes mono- and di-alkylated phenols in which each alkyl substituent contains from about 6 to about 100 carbon atoms, preferably about 6 to about 50 carbon atoms.

Illustrative alkyl phenols include heptylphenols, octylphenols, decylphenols, dodecylphenols, polypropylene (Mn of about 150)-substituted phenols, polyisobutene (Mn of about 1200)-substituted phenols, 40 cyclohexyl phenols.

Also useful are condensation products of the above-described phenols with at least one lower aldehyde or ketone, the term "lower" denoting aldehydes and ketones containing not more than 7 carbon atoms. Suitable aldehydes include formaldehyde, acetaldehyde, propionaldehyde, the butyraldehydes, the valeraldehydes and benzaldehyde. Also suitable are aldehyde-yielding reagents such as paraformaldehyde, 45 trioxane, methylol, Methyl Formcel and paraldehyde. Formaldehyde and the formaldehyde-yielding reagents are especially preferred.

The sulfurized alkylphenols include phenol sulfides, disulfides or polysulfides. The sulfurized phenols can be derived from any suitable alkylphenol by technique known to those skilled in the art, and many sulfurized phenols are commercially available. The sulfurized alkylphenols may be prepared by reacting an 50 alkylphenol with elemental sulfur and/or a sulfur monohalide (e.g., sulfur monochloride). This reaction may be conducted in the presence of excess base to result in the salts of the mixture of sulfides, disulfides or poly sulfides that may be produced depending upon the reaction conditions. It is the resulting product of this reaction which is used in the preparation of component (E-2) in the present invention. U.S. Patents 2,971,940 and 4,309,293 disclose various sulfurized phenols which are illustrative of component (E-2-c).

55 The equivalent weight of component (E-2-c) is its molecular weight divided by the number of hydroxy groups per molecule.

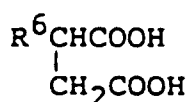
Component (E-2-d) is at least one oil-soluble carboxylic acid as previously described, or functional derivative thereof. Especially suitable carboxylic acids are those of the formula $R^5(COOH)_n$, wherein n is an

integer from 1 to 6 and is preferably 1 or 2 and R⁵ is a saturated or substantially saturated aliphatic group (preferably a hydrocarbon group) having at least 8 aliphatic carbon atoms. Depending upon the value of n, R⁵ will be a monovalent to hexavalent radical.

R⁵ may contain non-hydrocarbon substituents provided they do not alter substantially its hydrocarbon character. Such substituents are preferably present in amounts of not more than about 20% by weight. Exemplary substituents include the non-hydrocarbon substituents enumerated hereinabove with reference to component (E-2-a). R⁵ may also contain olefinic unsaturation up to a maximum of about 5% and preferably not more than 2% olefinic linkages based upon the total number of carbon-to-carbon covalent linkages present. The number of carbon atoms in R⁵ is usually about 8-700 depending upon the source of R⁵. As discussed below, a preferred series of carboxylic acids and derivatives is prepared by reacting an olefin polymer or halogenated olefin polymer with an alpha,beta-unsaturated acid or its anhydride such as acrylic, methacrylic, maleic or fumaric acid or maleic anhydride to form the corresponding substituted acid or derivative thereof. The R⁵ groups in these products have a number average molecular weight from about 150 to about 10,000 and usually from about 700 to about 5000, as determined, for example, by gel permeation chromatography.

The monocarboxylic acids useful as component (E-2-d) have the formula R⁵COOH. Examples of such acids are caprylic, capric, palmitic, stearic, isostearic, linoleic and behenic acids. A particularly preferred group of monocarboxylic acids is prepared by the reaction of a halogenated olefin polymer, such as a chlorinated polybutene, with acrylic acid or methacrylic acid.

Suitable dicarboxylic acids include the substituted succinic acids having the general formula



wherein R⁶ is the same as R⁵ as defined above. R⁶ may be an olefin polymer-derived group formed by polymerization of such monomers as ethylene, propylene, 1-butene, isobutene, 1-pentene, 2-pentene, 1-hexene and 3-hexene. R⁶ may also be derived from a high molecular weight substantially saturated petroleum fraction. The hydrocarbon-substituted succinic acids and their derivatives constitute the most preferred class of carboxylic acids for use as component (E-2-d).

The above-described classes of carboxylic acids derived from olefin polymers, and their derivatives, are well known in the art, and methods for their preparation as well as representative examples of the types useful in the present invention are described in detail in a number of U.S. Patents.

Functional derivatives of the above-discussed acids useful as component (E-2-d) include the anhydrides, esters, amides, imides, amidines and metal or ammonium salts. The reaction products of olefin polymer-substituted succinic acids and mono or polyamines, particularly polyalkylene polyamines, having up to about 10 amino nitrogens are especially suitable. These reaction products generally comprise mixtures of one or more of amides, imides and amidines. The reaction products of polyethylene amines containing up to about 10 nitrogen atoms and polybutene substituted succinic anhydride wherein the polybutene radical comprises principally isobutene units are particularly useful. Included in this group of functional derivatives are the compositions prepared by post treating the amine-anhydride reaction product with carbon disulfide, boron compounds, nitriles, urea, thiourea, guanidine, alkylene oxides or the like. The half-amide, half-metal salt and half-ester, half-metal salt derivatives of such substituted succinic acids are also useful.

Also useful are the esters prepared by the reaction of the substituted acids or anhydrides with a mono or polyhydroxy compound, such as an aliphatic alcohol or a phenol. Preferred are the esters of olefin polymer-substituted succinic acids or anhydrides and polyhydric aliphatic alcohols containing 2-10 hydroxy groups and up to about 40 aliphatic carbon atoms. This class of alcohols includes ethylene glycol, glycerol, sorbitol, pentaerythritol, polyethylene glycol, diethanolamine, triethanolamine, N,N'-di(hydroxyethyl)-ethylenediamine and the like. When the alcohol contains reactive amino groups, the reaction product may comprise products resulting from the reaction of the acid group with both the hydroxy and amino functions. Thus, this reaction mixture can include half-esters, half-amides, esters, amides, and imides.

The ratios of equivalents of the constituents of reagent (E-2) may vary widely. In general, the ratio of component (E-2-b) to (E-2-a) is at least about 4:1 and usually not more than about 40:1, preferably between 6:1 and 30:1 and most preferably between 8:1 and 25:1. While this ratio may sometimes exceed 40:1, such an excess normally will serve no useful purpose.

The ratio of equivalents of component (E-2-c) to component (E-2-a) is between about 1:20 and 80:1, and preferably between about 2:1 and 50:1. As mentioned above, when component (E-2-c) is an alkyl phenol or sulfurized alkyl phenol, the inclusion of the carboxylic acid (E-2-d) is optional. When present in the mixture, the ratio of equivalents of component (E-2-d) to component (E-2-a) generally is from about 1:1 to about 1:20 and preferably from about 1:2 to about 1:10.

Up to about a stoichiometric amount of acidic material (E-1) is reacted with (E-2). In one embodiment, the acidic material is metered into the (E-2) mixture and the reaction is rapid. The rate of addition of (E-1) is not critical, but may have to be reduced if the temperature of the mixture rises too rapidly due to the exothermicity of the reaction.

When (E-2-c) is an alcohol, the reaction temperature is not critical. Generally, it will be between the solidification temperature of the reaction mixture and its decomposition temperature (i.e., the lowest decomposition temperature of any component thereof). Usually, the temperature will be from about 25 °C to about 200 °C and preferably from about 50 °C to about 150 °C. Reagents (E-1) and (E-2) are conveniently contacted at the reflux temperature of the mixture. This temperature will obviously depend upon the boiling points of the various components; thus, when methanol is used as component (E-2-c), the contact temperature will be at or below the reflux temperature of methanol.

When reagent (E-2-c) is an alkyl phenol or a sulfurized alkyl phenol, the temperature of the reaction must be at or above the water azeotrope temperature so that the water formed in the reaction can be removed.

The reaction is ordinarily conducted at atmospheric pressure, although superatmospheric pressure often expedites the reaction and promotes optimum utilization of reagent (E-1). The reaction also can be carried out at reduced pressures but, for obvious practical reasons, this is rarely done.

The reaction is usually conducted in the presence of a substantially inert, normally liquid organic diluent, which functions as both the dispersing and reaction medium. This diluent will comprise at least about 10% of the total weight of the reaction mixture.

Upon completion of the reaction, any solids in the mixture are preferably removed by filtration or other conventional means. Optionally, readily removable diluents, the alcoholic promoters, and water formed during the reaction can be removed by conventional techniques such as distillation. It is usually desirable to remove substantially all water from the reaction mixture since the presence of water may lead to difficulties in filtration and to the formation of undesirable emulsions in fuels and lubricants. Any such water present is readily removed by heating at atmospheric or reduced pressure or by azeotropic distillation. In one preferred embodiment, when basic potassium sulfonates are desired as component (E), the potassium salt is prepared using carbon dioxide and the sulfurized alkylphenols as component (E-2-c). The use of the sulfurized phenols results in basic salts of higher metal ratios and the formation of more uniform and stable salts.

The basic salts or complexes of component (E) may be solutions or, more likely, stable dispersions. Alternatively, they may be regarded as "polymeric salts" formed by the reaction of the acidic material, the oil-soluble acid being overbased, and the metal compound. In view of the above, these compositions are most conveniently defined by reference to the method by which they are formed.

The above-described procedure for preparing alkali metal salts of sulfonic acids having a metal ratio of at least about 2 and preferably a metal ratio between about 4 to 40 using alcohols as component (E-2-c) is described in more detail in Canadian Patent 1,055,700 which corresponds to British Patent 1,481,553. The preparation of oil-soluble dispersions of alkali metal sulfonates useful as component (E) in the lubricating oil compositions of this invention is illustrated further in the following examples.

Example E-1

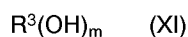
To a solution of 790 parts (1 equivalent) of an alkylated benzenesulfonic acid and 71 parts of polybutenyl succinic anhydride (equivalent weight about 560) containing predominantly isobutene units in 176 parts of mineral oil is added 320 parts (8 equivalents) of sodium hydroxide and 640 parts (20 equivalents) of methanol. The temperature of the mixture increases to 89 °C (reflux) over 10 minutes due to exotherming. During this period, the mixture is blown with carbon dioxide at 4 cfh. (cubic feet/hr.) (113.2 liters/hour). Carbonation is continued for about 30 minutes as the temperature gradually decreases to 74 °C. The methanol and other volatile materials are stripped from the carbonated mixture by blowing nitrogen through it at 2 cfh (56.6 liters/hour). while the temperature is slowly increased to 150 °C over 90 minutes. After stripping is completed, the remaining mixture is held at 155-165 °C for about 30 minutes and filtered to yield an oil solution of the desired basic sodium sulfonate having a metal ratio of about 7.75. This solution contains 12.4% oil.

Example E-2

Following the procedure of Example E-1, a solution of 780 parts (1 equivalent) of an alkylated benzenesulfonic acid and 119 parts of the polybutenyl succinic anhydride in 442 parts of mineral oil is mixed with 800 parts (20 equivalents) of sodium hydroxide and 704 parts (22 equivalents) of methanol. The mixture is blown with carbon dioxide at 7 cfh (198.1 liters/hour). for 11 minutes as the temperature slowly increases to 97°C. The rate of carbon dioxide flow is reduced to 6 cfh (169.8 liters/hour). and the temperature decreases slowly to 88°C over about 40 minutes. The rate of carbon dioxide flow is reduced to 5 cfh. (141.5 liters/hour) for about 35 minutes and the temperature slowly decreases to 73°C. The volatile materials are stripped by blowing nitrogen through the carbonated mixture at 2 cfh (56.6 liters/hour). for 105 minutes as the temperature is slowly increased to 160°C. After stripping is completed, the mixture is held at 160°C for an additional 45 minutes and then filtered to yield an oil solution of the desired basic sodium sulfonate having a metal ratio of about 19.75. This solution contains 18.7% oil.

(F) Carboxylic Ester Derivative Compositions.

The lubricating oil compositions of the present invention also may, and often do contain (F) at least one carboxylic ester derivative composition produced by reacting (F-1) at least one substituted succinic acylating agent with (F-2) at least one alcohol or phenol of the general formula



wherein R^3 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. The carboxylic ester derivatives (F) are included in the oil compositions in amounts of up to about 10% by weight and more generally in amounts of from about 1% to about 10% by weight based on the weight of the total lubricating oil. The carboxylic esters (F) provide additional dispersancy, and in some applications, the ratio of carboxylic derivative (B) to carboxylic ester (F) present in the oil affects the properties of the oil compositions such as the anti-wear properties. The amount of carboxylic ester derivative (F) contained in the lubricating oil composition may vary from about 0.1% to about 10% by weight.

The substituted succinic acylating agents (F-1) which are reacted with the alcohols or phenols to form the carboxylic ester derivatives are identical to the acylating agents (B-1) useful in preparing the carboxylic derivatives (B) described above with one exception. The polyalkene from which the substituent is derived is characterized as having a number average molecular weight of at least about 700.

Molecular weights (M_n) of from about 700 to about 5000 are preferred. In one preferred embodiment, the substituent groups of the acylating agent are derived from polyalkenes which are characterized by an M_n value of about 1300 to 5000 and an M_w/M_n value of about 1.5 to about 4.5. The acylating agents of this embodiment are identical to the acylating agents described earlier with respect to the preparation of the carboxylic derivative compositions useful as component (B) described above. Thus, any of the acylating agents described in regard to the preparation of component (B) above, can be utilized in the preparation of the carboxylic ester derivative compositions useful as component (F). When the acylating agents used to prepare the carboxylic ester (F) are the same as those acylating agents used for preparing component (B), the carboxylic ester component (F) will also be characterized as a dispersant having VI properties. Also combinations of component (B) and these preferred types of component (F) used in the oils of the invention provide superior anti-wear characteristics to the oils of the invention. However, other substituted succinic acylating agents also can be utilized in the preparation of the carboxylic ester derivative compositions which are useful as component (F) in the present invention. For example, substituted succinic acylating agents wherein the substituent is derived from a polyalkene having number average molecular weights of about 800 to about 1200 are useful.

The carboxylic ester derivative compositions (F) are those of the above-described succinic acylating agents with hydroxy compounds which 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-dibutylphenol, etc.

The alcohols (F-2) from which the esters may be derived preferably contain up to about 40 aliphatic carbon atoms. They may be monohydric alcohols such as methanol, ethanol, isooctanol, dodecanol, cyclohexanol, etc. The polyhydric alcohols preferably contain from 2 to about 10 hydroxy groups. They are illustrated by, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol,

dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols in which the alkylene group contains from 2 to about 8 carbon atoms.

An especially preferred class of polyhydric alcohols is those having at least three hydroxy groups, some of which have been esterified with a monocarboxylic acid having from about 8 to about 30 carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid, or tall oil acid. Examples of such partially esterified polyhydric alcohols are the monooleate of sorbitol, distearate of sorbitol, monooleate of glycerol, monostearate of glycerol, di-dodecanoate of erythritol.

The esters (F) may be prepared by any of several known methods. The method which is preferred because of convenience and the superior properties of the esters it produces, involves the reaction of a suitable alcohol or phenol with a substantially hydrocarbon-substituted succinic anhydride. The esterification is usually carried out at a temperature above about 100°C, preferably between 150°C and 300°C. The water formed as a by-product is removed by distillation as the esterification proceeds.

The relative proportions of the succinic reactant and the hydroxy reactant which are to be used depend to a large measure upon the type of the product desired and the number of hydroxyl groups present in the molecule of the hydroxy reactant. For instance, the formation of a half ester of a succinic acid, i.e., one in which only one of the two acid groups is esterified, involves the use of one mole of a monohydric alcohol for each mole of the substituted succinic acid reactant, whereas the formation of a diester of a succinic acid involves the use of two moles of the alcohol for each mole of the acid. On the other hand, one mole of a hexahydric alcohol may combine with as many as six moles of a succinic acid to form an ester in which each of the six hydroxyl groups of the alcohol is esterified with one of the two acid groups of the succinic acid. Thus, the maximum proportion of the succinic acid to be used with a polyhydric alcohol is determined by the number of hydroxyl groups present in the molecule of the hydroxy reactant. In one embodiment, esters obtained by the reaction of equimolar amounts of the succinic acid reactant and hydroxy reactant are preferred.

Methods of preparing the carboxylic esters (F) are well known in the art and need not be illustrated in further detail here. For example, see U.S. Patent 3,522,179 discloses the preparation of carboxylic ester compositions useful as component (F). The preparation of carboxylic ester derivative compositions from acylating agents wherein the substituent groups are derived from polyalkenes characterized by an Mn of at least about 1300 up to about 5000 and an Mw/Mn ratio of from 1.5 to about 4 is described in U.S. Patent 4,234,435. As noted above, the acylating agents described in the '435 patent are also characterized as having within their structure an average of at least 1.3 succinic groups for each equivalent weight of substituent groups.

The following examples illustrate the esters (F) and the processes for preparing such esters.

Example F-1

A substantially hydrocarbon-substituted succinic anhydride is prepared by chlorinating a polyisobutene having a number average molecular weight of 1000 to a chlorine content of 4.5% and then heating the chlorinated polyisobutene with 1.2 molar proportions of maleic anhydride at a temperature of 150-220°C. The succinic anhydride thus obtained has an acid number of 130. A mixture of 874 grams (1 mole) of the succinic anhydride and 104 grams (1 mole) of neopentyl glycol is maintained at 240-250°C/30 mmHg for 12 hours. The residue is a mixture of the esters resulting from the esterification of one and both hydroxy groups of the glycol. It has a saponification number of 101 and an alcoholic hydroxyl content of 0.2%.

Example F-2

The dimethyl ester of the substantially hydrocarbon-substituted succinic anhydride of Example F-1 is prepared by heating a mixture of 2185 grams of the anhydride, 480 grams of methanol, and 1000 ml of toluene at 50-65°C while hydrogen chloride is bubbled through the reaction mixture for 3 hours. The mixture is then heated at 60-65°C for 2 hours, dissolved in benzene, washed with water, dried and filtered. The filtrate is heated at 150°C/60 mmHg to remove volatile components. The residue is the desired dimethyl ester.

The carboxylic ester derivatives which are described above resulting from the reaction of an acylating agent with a hydroxy containing compound such as an alcohol or a phenol may be further reacted with (F-3) an amine, and particularly polyamines in the manner described previously for the reaction of the acylating agent (B-1) with amines (B-2) in preparing component (B). In one embodiment, the amount of amine which is reacted with the ester is an amount such that there is at least about 0.01 equivalent of the amine for each equivalent of acylating agent initially employed in the reaction with the alcohol. Where the acylating agent

has been reacted with the alcohol in an amount such that there is at least one equivalent of alcohol for each equivalent of acylating agent, this small amount of amine is sufficient to react with minor amounts of non-esterified carboxyl groups which may be present. In one preferred embodiment, the amine-modified carboxylic acid esters utilized as component (F) are prepared by reacting about 1.0 to 2.0 equivalents, preferably about 1.0 to 1.8 equivalents of hydroxy compounds, and up to about 0.3 equivalent, preferably 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 carboxylic ester derivative compositions which are useful as component (F) 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. The following specific examples illustrate the preparation of the esters wherein both alcohols and amines are reacted with the acylating agent.

Example F-3

A mixture of 334 parts (0.52 equivalent) of the polyisobutene-substituted succinic acylating agent prepared in Example F-2, 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier from Dow Chemical Company is heated at 150 °C for 2.5 hours. The reaction mixture is heated to 210 °C in 5 hours and held at 210 °C for 3.2 hours. The reaction mixture is cooled to 190 °C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an average of about 3 to about 10 nitrogen atoms per molecule are added. The reaction mixture is stripped by heating at 205 °C with nitrogen blowing for 3 hours, then filtered to yield the filtrate as an oil solution of the desired product.

Example F-4

A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared in Example F-2, 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227 °C for 5 hours. The reaction mixture is cooled to 162 °C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an average of about 3 to 10 nitrogen atoms per molecule is added. The reaction mixture is heated at 162-163 °C for one hour, then cooled to 130 °C and filtered. The filtrate is an oil solution of the desired product.

Example F-5

A mixture of 1000 parts (0.495 mole) of polyisobutene having a number average molecular weight of 2020 and a weight average molecular weight of 6049 and 115 parts (1.17 moles) of maleic anhydride is heated to 184 °C over 6 hours, during which time 85 parts (1.2 moles) of chlorine are added beneath the surface. An additional 59 parts (0.83 mole) of chlorine are added over 4 hours at 184-189 °C. The mixture is blown with nitrogen at 186-190 °C for 26 hours. The residue is a polyisobutene-substituted succinic anhydride having a total acid number of 95.3.

A solution of 409 parts (0.66 equivalent) of the substituted succinic anhydride in 191 parts of mineral oil is heated to 150 °C and 42.5 parts (1.19 equivalent) of pentaerythritol are added over 10 minutes, with stirring, at 145-150 °C. The mixture is blown with nitrogen and heated to 205-210 °C over about 14 hours to yield an oil solution of the desired polyester intermediate.

Diethylene triamine, 4.74 parts (0.138 equivalent), is added over one-half hour at 160 °C with stirring, to 988 parts of the polyester intermediate (containing 0.69 equivalent of substituted succinic acylating agent and 1.24 equivalents of pentaerythritol). Stirring is continued at 160 °C for one hour, after which 289 parts of mineral oil are added. The mixture is heated for 16 hours at 135 °C and filtered at the same temperature, using a filter aid material. The filtrate is a 35% solution in mineral oil of the desired aminemodified polyester. It has a nitrogen content of 0.16% and a residual acid number of 2.0.

Example F-6

(a) A mixture of 1000 parts of polyisobutene having a number average molecular weight of about 1000 and 108 parts (1.1 moles) of maleic anhydride is heated to about 190 °C and 100 parts (1.43 moles) of chlorine are added beneath the surface over a period of about 4 hours while maintaining the temperature

at about 185-190 °C. The mixture then is blown with nitrogen at this temperature for several hours, and the residue is the desired polyisobutene-substituted succinic acylating agent.

(b) A solution of 1000 parts of the acylating agent preparation (a) in 857 parts of mineral oil is heated to about 150 °C with stirring, and 109 parts (3.2 equivalents) of pentaerythritol are added with stirring. The mixture is blown with nitrogen and heated to about 200 °C over a period of about 14 hours to form an oil solution of the desired carboxylic ester intermediate. To the intermediate, there are added 19.25 parts (.46 equivalent) of a commercial mixture of ethylene polyamines having an average of about 3 to about 10 nitrogen atoms per molecule. The reaction mixture is stripped by heating at 205 °C with nitrogen blowing for 3 hours and filtered. The filtrate is an oil solution (45% oil) of the desired amine-modified carboxylic ester which contains 0.35% nitrogen.

Example F-7

(a) A mixture of 1000 parts (0.495 mole) of polyisobutene having a number average molecular weight of 2020 and a weight average molecular weight of 6049 and 115 parts (1.17 moles) of maleic anhydride is heated to 184 °C over 6 hours, during which time 85 parts (1.2 moles) of chlorine are added beneath the surface. An additional 59 parts (0.83 mole) of chlorine are added over 4 hours at 184-189 °C. The mixture is blown with nitrogen at 186-190 °C for 26 hours. The residue is a polyisobutene-substituted succinic anhydride having a total acid number of 95.3.

(b) A solution of 409 parts (0.66 equivalent) of the substituted succinic anhydride in 191 parts of mineral oil is heated to 150 °C and 42.5 parts (1.19 equivalent) of pentaerythritol are added over 10 minutes, with stirring, at 145-150 °C. The mixture is blown with nitrogen and heated to 205-210 °C over about 14 hours to yield an oil solution of the desired polyester intermediate.

Diethylene triamine, 4.74 parts (0.138 equivalent), is added over one-half hour at 160 °C with stirring, to 988 parts of the polyester intermediate (containing 0.69 equivalent of substituted succinic acylating agent and 1.24 equivalents of pentaerythritol). Stirring is continued at 160 °C for one hour, after which 289 parts of mineral oil are added. The mixture is heated for 16 hours at 135 °C and filtered at the same temperature, using a filter aid material. The filtrate is a 35% solution in mineral oil of the desired amine-modified polyester. It has a nitrogen content of 0.16% and a residual acid number of 2.0.

The lubricating oil compositions of the present invention also may contain, and preferably do contain, other additives to impart certain desirable properties to the lubricant. For example, the oils may contain at least one friction modifier to provide the lubricating oil with the proper frictional characteristics. Various amines, particularly tertiary amines are effective friction modifiers. Examples of tertiary amine friction modifiers include N-fatty alkyl-N,N-diethanol amines, N-fatty alkyl-N,N-diethoxy ethanol amines, etc. Such tertiary amines can be prepared by reacting a fatty alkyl amine with an appropriate number of moles of ethylene oxide. Tertiary amines derived from naturally occurring substances such as coconut oil and oleoamine are available from Armour Chemical Company under the trade designation "Ethomeen". Particular examples are the Ethomeen-C and the Ethomeen-O series.

Sulfur-containing compounds such as sulfurized C₁₂₋₂₄ fats, alkyl sulfides and polysulfides wherein the alkyl groups contain from 1 to 8 carbon atoms, and sulfurized polyolefins also may function as friction modifiers in the lubricating oil compositions of the invention.

In one embodiment, a preferred friction modifier to be included in the lubricating oil compositions of the present invention is at least one partial fatty acid ester of a polyhydric alcohol, and generally, up to about 1% by weight of the partial fatty acid esters appears to provide the desired friction-modifying characteristics. The hydroxy fatty acid esters are selected from hydroxy fatty acid esters of dihydric or polyhydric alcohols or oil-soluble oxyalkylenated derivatives thereof.

Suitable partial fatty acid esters of polyhydric alcohols include, for example, glycol monoesters, glycerol mono- and diesters, and pentaerythritol di- and/or triesters. The partial fatty acid esters of glycerol are preferred, and of the glycerol esters, monoesters, or mixtures of monoesters and diesters are often utilized. The partial fatty acid esters of polyhydric alcohols can be prepared by methods well known in the art, such as by direct esterification of an acid with a polyol, reaction of a fatty acid with an epoxide, etc.

It is generally preferred that the partial fatty acid ester contain olefinic unsaturation, and this olefinic unsaturation usually is found in the acid moiety of the ester. In addition to natural fatty acids containing olefinic unsaturation such as oleic acid, octeneoic acids, tetradeceneoic acids, etc., can be utilized in forming the esters.

The partial fatty acid esters utilized as friction modifiers in the lubricating oil compositions of the present invention may be present as components of a mixture containing a variety of other components such as unreacted fatty acid, fully esterified polyhydric alcohols, and other materials. Commercially

available partial fatty acid esters often are mixtures which contain one or more of these components as well as mixtures of mono- and diesters of glycerol.

Among the commercially available glycerol esters are ester mixtures containing at least about 30% by weight of monoester and generally from about 35% to about 65% by weight of monoester, about 30% to about 50% by weight of diester, and the balance in the mixture, generally less than about 15%, is a mixture of triesters, free fatty acids and other components. Specific examples of commercially available material comprising fatty acid esters of glycerol include Emery 2421 (Emery Industries, Inc.), Cap City GMO (Capital), DUR-EM 114, DUR-EM GMO, etc. (Durkee Industrial Foods, Inc.) and various materials identified under the mark MAZOL GMO (Mazer Chemicals, Inc.). Other examples of partial fatty acid esters of polyhydric alcohols may be found in K.S. Markley, Ed., "Fatty Acids", Second Edition, Parts I and V, Interscience Publishers (1968). Numerous commercially available fatty acid esters of polyhydric alcohols are listed by tradename and manufacturer in McCutcheons' Emulsifiers and Detergents, North American and International Combined Editions (1981).

The lubricating oil compositions of the present invention also may contain at least one neutral or basic alkaline earth metal salt of at least one acidic organic compound. Such salt compounds generally are referred to as ash-containing detergents. The acidic organic compound may be at least one sulfur acid, carboxylic acid, phosphorus acid, or phenol, or mixtures thereof. Generally, the basic or overbased salts are preferred. The basic or overbased salts will have metal ratios of up to about 40 and more particularly from about 2 to about 30 or 40.

Calcium, magnesium, barium and strontium are the preferred alkaline earth metals. Salts containing a mixture of ions of two or more of these alkaline earth metals can be used.

A commonly employed method for preparing the basic (or overbased) salts comprises heating a mineral oil solution of the acid with a stoichiometric excess of a metal neutralizing agent, e.g., a metal oxide, hydroxide, carbonate, bicarbonate, sulfide, etc., at temperatures above about 50 °C. In addition, various promoters may be used in the neutralizing process to aid in the incorporation of the large excess of metal. These promoters include such compounds as the phenolic substances, e.g., phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol and the various condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecyl amine, etc. A particularly effective process for preparing the basic salts comprises mixing the acid with an excess of the basic alkaline earth metal in the presence of the phenolic promoter and a small amount of water and carbonating the mixture at an elevated temperature, e.g., 60 °C to about 200 °C.

As mentioned above, the acidic organic compound from which the salt alkaline earth metal is derived may be at least one sulfur acid, carboxylic acid, phosphorus acid, or phenol or mixtures thereof. Some of these acidic organic compounds (sulfonic and carboxylic acids) previously have been described above with respect to the preparation of the alkali metal salts (component (E)), and all of the acidic organic compounds described above can be utilized in the preparation of the alkaline earth metal salts. In addition to the sulfonic acids, the sulfur acids include thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acids.

The pentavalent phosphorus acids may be an organophosphoric, phosphonic or phosphinic acid, or a thio analog of any of these.

The alkaline earth metal salts may also be prepared from phenols; that is, compounds containing a hydroxy group bound directly to an aromatic ring. The term "phenol" as used herein includes compounds having more than one hydroxy group bound to an aromatic ring, such as catechol, resorcinol and hydroquinone. It also includes alkylphenols such as the cresols and ethylphenols, and alkenylphenols. Preferred are phenols containing at least one alkyl substituent containing about 3-100 and especially about 6-50 carbon atoms, such as heptylphenol, octylphenol, dodecylphenol, tetrapropene-alkylated phenol, octadecylphenol and polybutenyl-phenols. Phenols containing more than one alkyl substituent may also be used, but the monoalkylphenols are preferred because of their availability and ease of production.

Also useful are condensation products of the above-described phenols with at least one lower aldehyde or ketone, the term "lower" denoting aldehydes and ketones containing not more than 7 carbon atoms. Suitable aldehydes include formaldehyde, acetaldehyde, propionaldehyde, etc.

The amount of alkaline earth metal salt included in the lubricants of the present invention also may be varied over a wide range, and useful amounts in any particular lubricating oil composition can be readily determined by one skilled in the art. The salts function as auxiliary or supplemental detergent. The amount contained in a lubricant of the invention may vary from about 0% to about 5% or more.

The lubricating oils of the invention may contain at least one neutral or basic alkaline earth metal salt of an alkylphenol sulfide. The oils may contain from about 0 to about 2 or 3% of said phenol sulfides. More often, the oil may contain from about 0.01 to about 2% by weight of the basic salts of phenol sulfides. The term "basic" is used herein the same way in which it was used in the definition of other components above.

5 The neutral and basic salts of phenol sulfides provide antioxidant and detergent properties of the oil compositions of the invention.

The oil compositions of the present invention also may contain one or more sulfur-containing composition useful in improving the antiwear, extreme pressure and antioxidant properties of the lubricating oil compositions. Sulfur-containing compositions prepared by the sulfurization of various organic materials including olefins are useful. The olefins may be any aliphatic, arylaliphatic or alicyclic olefinic hydrocarbon containing from about 3 to about 30 carbon atoms.

U.S. Patents 4,119,549, 4,505,830 refer to suitable sulfurized olefins useful in the lubricating oils of the present invention. Several specific sulfurized compositions are described in the working examples thereof.

Other extreme pressure agents and corrosion- and oxidation-inhibiting agents also may be included and are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid and sulfurized alkylphenol; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See, for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith, Lezius-Hiles Co. publishers, Cleveland, Ohio, 1967.

Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers 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.

35 Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents" by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

The lubricating oil compositions of the present invention also may contain, particularly when the lubricating oil compositions are formulated into multigrade oils, one or more commercially available viscosity modifiers. Viscosity modifiers generally are polymeric materials characterized as being hydrocarbon-based polymers generally having number average molecular weights between about 25,000 and 500,000 more often between about 50,000 and 200,000.

Polyisobutylene has been used as a viscosity modifier in lubricating oils. Polymethacrylates (PMA) are prepared from mixtures of methacrylate monomers having different alkyl groups. Most PMA's are viscosity-modifiers as well as pour point depressants. The alkyl groups may be either straight chain or branched chain groups containing from 1 to about 18 carbon atoms.

When a small amount of a nitrogen-containing monomer is copolymerized with alkyl methacrylates, dispersancy properties also are incorporated into the product. Thus, such a product has the multiple function of viscosity modification, pour point depressants and dispersancy. Such products have been referred to in the art as dispersant-type viscosity modifiers or simply dispersant-viscosity modifiers. Vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers. Polyacrylates obtained from the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity-modifiers.

Ethylene-propylene copolymers, generally referred to as OCP can be prepared by copolymerizing ethylene and propylene, generally in a solvent, using known catalysts such as a Ziegler-Natta initiator. The ratio of ethylene to propylene in the polymer influences the oil-solubility, oil-thickening ability, low temperature viscosity, pour point depressant capability and engine performance of the product. The common range of ethylene content is 45-60% by weight and typically is from 50% to about 55% by weight.

Some commercial OCP's are terpolymers of ethylene, propylene and a small amount of non-conjugated diene such as 1,4-hexadiene. In the rubber industry, such terpolymers are referred to as EPDM (ethylene propylene diene monomer). The use of OCP's as viscosity modifiers in lubricating oils has increased rapidly since about 1970, and the OCP's are currently one of the most widely used viscosity modifiers for motor oils.

Esters obtained by copolymerizing styrene and maleic anhydride in the presence of a free radical initiator and thereafter esterifying the copolymer with a mixture of C_4-18 alcohols also are useful as viscosity modifying additives in motor oils. The styrene esters generally are considered to be multifunctional premium viscosity modifiers. The styrene esters in addition to their viscosity modifying properties also are pour point depressants and exhibit dispersancy properties when the esterification is terminated before its completion leaving some unreacted anhydride or carboxylic acid groups. These acid groups can then be converted to imides by reaction with a primary amine. Hydrogenated styrene-conjugated diene copolymers are another class of commercially available viscosity modifiers for motor oils.

The above described hydrogenated copolymers have been described in the prior art such as in U.S. Patents 3,551,336; 3,598,738; 3,554,911; 3,607,749; 3,687,849; and 4,181,618. Their disclosures refer to polymers and copolymers useful as viscosity modifiers in the oil compositions of this invention. Hydrogenated styrene-butadiene copolymers useful as viscosity modifiers in the lubricating oil compositions of the present invention are available commercially from, for example, BASF under the general trade designation "Glissoviscal". A particular example is a hydrogenated styrene-butadiene copolymer available under the designation Glissoviscal 5260 which has a molecular weight, determined by gel permeation chromatography, of about 120,000. Hydrogenated styrene-isoprene copolymers useful as viscosity modifiers are available from, for example, The Shell Chemical Company under the general trade designation "Shellvis". Shellvis 40 from Shell Chemical Company is identified as a diblock copolymer of styrene and isoprene having a number average molecular weight of about 155,000, a styrene content of about 19 mole percent and an isoprene content of about 81 mole percent. Shellvis 50 is available from Shell Chemical Company and is identified as a diblock copolymer of styrene and isoprene having a number average molecular weight of about 100,000, a styrene content of about 28 mole percent and an isoprene content of about 72 mole percent. Generally, the polymeric viscosity improvers are used in concentrations of about 0.2 to about 8% and more particularly, in amounts from about 0.5 to about 6% by weight of the finished lubricating oil.

The lubricating oils of the present invention may be prepared by dissolving or suspending the various components directly in a base oil along with any other additives which may be used. More often, the chemical components of the present invention are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, etc. to form an additive concentrate. These concentrates usually comprise from about 0.01 to about 80% by weight of one or more of the additive components (A) through (C) described above, and may contain, in addition, one or more of the other additives described above. Chemical concentrations such as 15%, 20%, 30% or 50% or higher may be employed.

For example, concentrates may contain on a chemical basis, from about 10 to about 50% by weight of the carboxylic derivative composition (B), and from about 10 to about 5000 ppm of manganese as metal. The concentrates also may contain from about 0.01% to about 15% of the metal phosphorodithioates (D), from about 1 to about 30% by weight of the carboxylic ester (F) and/or from about 1% to about 20% by weight of at least one neutral or basic alkali metal salt (F).

Typical lubricating oil compositions according to the present invention are exemplified in the following lubrication oil examples wherein the percentages are on a volume basis and the percentages indicate the amount of the normally oil diluted solutions of the indicated additives used to form the lubricating oil composition. For example, Lubricant I contains 3.5% by volume of the product of Example B-10 which is an oil solution of the indicated carboxylic derivative (B) containing 55% diluent oil.

Lubricant Example I	
Components	Percent
Product of Ex. B-10	3.5
Product of Ex. D-1	0.4
Zinc salt of a phosphorodithioic acid prepared from amyl and isobutyl alcohol mixture (35:65)m	0.47
Product of Ex. E-1	0.25
Basic magnesium alkylated benzene sulfonate	0.33
Basic calcium alkylated benzene sulfonate	0.41
Overbased manganese carboxylate (40% Mn) (Mooney FOA-910)	250 ppm
Amide-based friction modifier	0.1
C ₉ mono- and C ₉ -di-para-alkylated diphenylamine	0.1
Sulfurized butyl acrylate-butadiene product	0.15
Silicone antifoam	0.006
Mineral oil	remainder

Lubricant Example II	
Components	Percent
Product of Ex. B-10	3.0
Zinc salt of diisooctyl phosphorodithioic acid	1.07
Product of Ex. F-6	2.8
Basic magnesium sulfonate	0.35
Basic calcium sulfonate	0.92
Nonyl phenoxy poly(ethyleneoxy) ethanol	0.1
Overbased manganese carboxylate (40% Mn) (Mooney FOA-910)	250 ppm
Propylene tetramer phenol reacted with sulfur dichloride	2.3
Silicone antifoam	0.001
Mineral oil	remainder

The lubricating oil compositions of the present invention exhibit a reduced tendency to deteriorate under conditions of use and thereby reduce wear and the formation of such undesirable deposits as varnish, sludge, carbonaceous materials and resinous materials which tend to adhere to the various engine parts and reduce the efficiency of the engines. In one embodiment, lubricating oils can be formulated within this invention which can pass all of the tests required for classification as an SG oil.

The lubrication oils of this invention are useful also in diesel engines, and lubricating oil formulations can be prepared in accordance with this invention which meet the requirements of the new diesel classification CE.

The performance characteristics of the lubricating oil compositions of the present invention are evaluated by subjecting lubricating oil compositions to a number of engine oil tests which have been designed to evaluate various performance characteristics of engine oils.

The ASTM Sequence IIID engine oil test simulates high speed, high load operation and is a severe test of an oil's ability to lubricate under demanding conditions. This test utilizes a production 5.7 liter, 2-barrel 8.5:1 compression Oldsmobile V-8 gasoline engine. Each test requires that the engine be built to the specific instructions outlined in ASTM STP 315H. The test is conducted in two parts consisting of a 4-hour break-in period followed by a 64-hour steady-state test period. The engine is operated at 100 bhp (74.6 kW) and 3000 rpm during the 64-hour test period. The test is monitored by sampling and analyzing the lubricant every 8 hours. New test oil is added to replenish the oil lost to sampling and blowby.

The performance criteria for the Sequence IIID test (SF Quality) are as follows: maximum viscosity increase measured at 45 °C after 64 hours = 375%; average engine sludge rating 9.2 minimum; average engine piston rating 9.2 minimum; average oil land deposits 4.8 minimum; cam and lifter wear (inches), average = 0.0040 (0.1016 mm), and maximum = 0.0080 (0.2032 mm); and oil consumption, quarts = 6.38

(6.06 l.). An inch corresponding to 25.4 mm and a quart \approx 0.95 l.

The results of the Sequence IIID test modified to use non-phosphated camshafts and conducted on Lubricants I and II and Control Lubricants I and II are summarized in the following table. Control Lubricants I and II are identical to Lubricants I and II respectively except that the Controls contain no manganese. (The normal Sequence IIID cam shafts are manganese phosphated to enhance scuffing resistance and to provide a lubricant reservoir in the contact zone.) Results of the tests are reported in the following table.

TABLE II
ASTM Sequence IIID Test Results

Test Lubricant	Non-Phosphated Camshafts		Non-Phosphated Camshafts	
	Cont-I	Cont-II	I	II
Average Sludge*	9.67	9.72	9.74	9.66
Average Piston Skirt Varnish*	9.15	9.32	9.32	9.34
Average Ring Land Deposits*	6.80	8.13	7.91	8.14
Cam Plus Lifter Wear (inches) [†]				
maximum	0.0005	0.0087	0.0006	0.0023
minimum	0.0001	0.0002	0.0003	0.0002
average	0.0003	0.0016	0.0004	0.0006
Viscosity Increase (%)				
64 hr.	283	44	36	50
Oil Consumption (qts.) ^{††}	4.84	4.67	3.97	4.55

* 10 - clean.

† an inch corresponds to 25.4 mm

†† a quart corresponds to \approx 0.95 liters

As mentioned above, in order for a lubricating oil to be qualified for API Service Classification SG, the lubricating oils must pass certain specified engine oil tests. However, lubricating oil compositions passing one or more of the individual tests also are useful in certain applications.

The ASTM Sequence IIIE engine oil test has been recently established as a means of defining the high-temperature wear, oil thickening, and deposit protection capabilities of SG engine oils. The IIIE test, which replaces the Sequence IIID test, provides improved discrimination with respect to high temperature camshaft and lifter wear protection and oil thickening control. The IIIE test utilizes a Buick 3.8L V-6 model

engine which is operated on leaded fuel at 67.8 bhp (50.58 kW) and 3000 rpm for a maximum test length of 64 hours. A valve spring load of 230 pounds (104.3 kg) is used. A 100% glycol coolant is used because of the high engine operating temperatures. Coolant outlet temperature is maintained at 118°C, and the oil temperature is maintained at 149°C at an oil pressure of 30 psi (2.1 kg/cm²). The air-to-fuel ratio is 16.5, and the blow-by rate is 1.6 cfm (45 l/m.). The initial oil charge is 146 ounces (4.14 kg)

The test is terminated when the oil level reaches 28 ounces (0.8 kg) low at any of the 8-hour check intervals. When the tests are concluded before 64 hours because of low oil level, the low oil level has generally resulted from hang-up of the heavily oxidized oil throughout the engine and its inability to drain to the oil pan at the 149°C oil check temperature. Viscosities are obtained on the 8-hour oil samples, and from this data, curves are plotted of percent viscosity increase versus engine hours. A maximum 375% viscosity increase measured at 40°C at 64 hours is required for API classification SG. The engine sludge requirement is a minimum rating of 9.2, the piston varnish a minimum of 8.9, and the ring land deposit a minimum of 3.5 based on the CRC merit rating system. Details of the current Sequence IIIE Test are contained in the "Sequence IIID Surveillance Panel Report on Sequence III Test to the ASTM Oil Classification Panel", dated November 30, 1987, revised January 11, 1988.

The results of the Sequence IIIE test conducted on Lubricants I and II are summarized in the following Table III. For comparison, results are also summarized for Control Oil I and Control Oil II which corresponded to Lubricants I and II, respectively except that the control oils do not contain the manganese additive.

TABLE III

ASTM Sequence III-E Test							
Lub.	Test Results						Oil Consumption (qts)*
		% Vis Increase	Engine Sludge	Piston Varnish	Ring Land Deposit	VTW ^a (VALUE TRAIN WEAR) Max/Min/Avg	
Cont I	I	3300	9.3	8.4	5.0	106/7/19	2.7
	I	210	9.6	8.9	6.3	12/7/9	1.9
Cont II	II	2400	9.2	8.8	3.7	1175/3/176	3.1
	II	740	9.3	9.0	4.5	133/6/70	3.6

a In ten-thousandths of an inch, wherein an inch = 25.4 mm.

* A quart corresponds to \approx 0.95 liters.

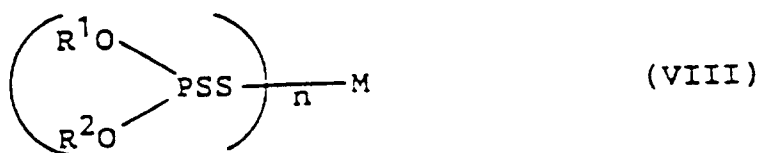
While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended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

Claims

1. A lubricating oil composition for internal combustion engines which comprises:
 - (A) a major amount of oil of lubricating viscosity;
 - (B) at least about 1.0% by weight of at least one carboxylic derivative composition produced by reacting
 - (B-1) at least one substituted succinic acylating agent with
 - (B-2) at least one amine compound characterized by the presence within its structure of at least one HN< group wherein said substituted succinic acylating agents consist of substituent groups and succinic groups wherein the substituent groups are derived from polyalkene, said polyalkene being characterized by an Mn value of 1300 to about 5000 and an Mw/Mn value of about 1.5 to about 4.5, said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups;

(C) at least one manganese compound in an amount corresponding to 1 to about 500 ppm of manganese; and

(D) from about 0.01% to about 5% by weight of a mixture of metal salts of dihydrocarbylphosphorodithioic acids wherein at least one metal dihydrocarbylphosphorodithioate is characterized by the general formula



wherein R¹ and R² are each independently hydrocarbyl groups containing from 3 to about 13 carbon atoms, M is a metal, and n is an integer equal to the valence of M wherein in at least one of the dihydrocarbylphosphorodithioic acids, one of the hydrocarbyl groups (D-1) is an isopropyl or secondary butyl group, the other hydrocarbyl group (D-2) contains at least 5 carbon atoms, and at least about 10 mole percent of all of the hydrocarbyl groups present in (D) are isopropyl groups, secondary butyl groups, or mixtures thereof.

2. The lubricating oil composition of claim 1 wherein at least one of R¹ and R² of (D) is attached to the oxygen atoms through a secondary carbon atom.

3. The lubricating oil composition of claim 1 wherein the manganese compound (C) is a salt of an acidic material selected from the group consisting of carboxylic acids, sulfonic acids, and phenols.

4. The lubricating oil composition of claim 1 wherein the manganese compound (C) is an overbased manganese salt of a mixture of carboxylic acids.

5. The lubricating oil composition of claim 1 containing the manganese compound (C) in an amount corresponding to about 50 to about 300 ppm of manganese.

6. The lubricating oil composition of claim 1 wherein the value of Mn in (B) is at least about 1500.

7. The lubricating oil composition of claim 1 wherein the value of Mw/Mn in (B) is at least about 2.0.

8. The lubricating oil composition of claim 1 wherein in (B), from about 0.5 equivalent up to about 2 moles of the amine (B-2) is reacted per equivalent of acylating agent (B-1).

9. The lubricating oil composition of claim 1 wherein the acylating agents (B-1) are characterized by the presence within their structure of at least about 1.5 up to about 2.5 succinic groups for each equivalent weight of the substituent groups.

10. The lubricating oil composition of claim 1, wherein the manganese compound (C) is at least one overbased manganese salt of a carboxylic or sulfonic acid in an amount corresponding to about 1 to about 500 ppm of manganese.

11. The lubricating oil composition of claim 1 or 10 which is substantially free of copper.

12. The lubricating oil composition of claim 1 or 10 wherein the manganese compound (C) is an overbased manganese carboxylate.

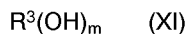
13. The lubricating oil composition of claim 1 or 10 also containing

(E) a detergent effective amount of at least one neutral or basic alkali metal salt of a sulfonic or carboxylic acid.

14. The lubricating oil composition of claim 13 wherein the alkali metal salt (E) is characterized as having a ratio of equivalents of alkali metal to equivalents of sulfonic or carboxylic acid of at least about 2:1.

15. The lubricating oil composition of claim 10 also containing

- (F) at least one carboxylic ester derivative composition produced by reacting
(F-1) at least one substituted succinic acylating agent with
(F-2) at least one alcohol of the general formula

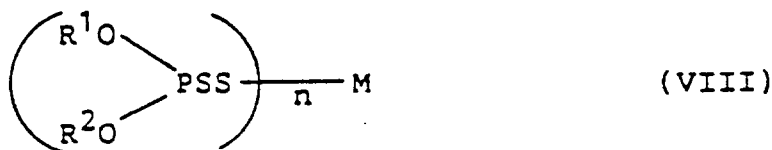


wherein R^3 is a monovalent or polyvalent organic group joined to the OH group, and m is an integer from 1 to about 10.

16. The lubricating oil composition of claim 15 wherein m is at least 2.

17. The lubricating oil composition of claim 15 wherein the composition obtained by reacting the acylating agent (F-1) with the alcohol (F-2) is further reacted with
(F-3) at least one amine containing at least one >NH group.

18. The lubricating oil composition of claim 1 wherein the manganese compound (C) is at least one overbased manganese salt of at least one carboxylic acid in an amount corresponding to about 50 to about 300 ppm of manganese; and the mixture of metal salts of dihydrocarbylphosphorodithioic acids (D) comprises from about 0.05% to about 5% by weight of at least one metal dihydrocarbylphosphorodithioate characterized by the general formula



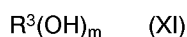
wherein R^1 and R^2 are each independently hydrocarbyl groups containing from 3 to about 13 carbon atoms, at least one of R^1 and R^2 is attached to the oxygen atom through a secondary carbon atom, M is a metal selected from the group consisting of Group II metals, aluminum, tin, iron, cobalt, lead, molybdenum, manganese, nickel or copper, and n is an integer equal to the valence of M.

19. The lubricating oil composition of claim 18 also containing

- (E) from about 0.01% to about 3% by weight of at least one neutral or basic alkali metal salt of a sulfonic or carboxylic acid.

20. The lubricating oil composition of claim 18 also containing

- (F) from about 0.1% to about 10% by weight of at least one carboxylic ester derivative composition produced by reacting
(F-1) at least one substituted succinic acylating agent with
(F-2) at least one alcohol of the general formula



wherein R^3 is a monovalent or polyvalent organic group joined to the OH group, and m is an integer from 1 to about 10.

21. A concentrate for formulating lubricating oil compositions comprising:

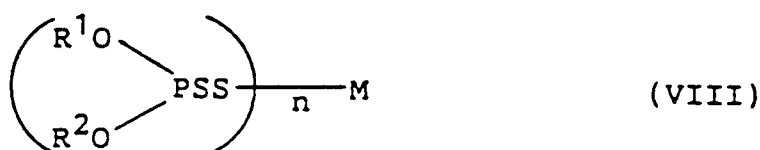
- (A) from about 20% to about 90% by weight of a normally liquid, substantially inert organic diluent/solvent;
(B) from about 10% to about 50% by weight of at least one carboxylic derivative composition produced by reacting

(B-1) at least one substituted succinic acylating agent with

(B-2) at least one amine compound characterized by the presence within its structure of at least one HN< group wherein said substituted succinic acylating agents consist of substituent groups and succinic groups wherein the substituent groups are derived from polyalkene, said polyalkene being characterized by an Mn value of 1300 to about 5000 and an Mw/Mn value of about 1.5 to about 4.5, said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups;

(C) at least one manganese compound in an amount corresponding to about 10 to about 5000 ppm of manganese provided that the manganese compound is not a neutral manganese dihydrocarbylphosphorodithioate; and

(D) from about 0.05% to about 15% by weight of a mixture of metal salts of dihydrocarbylphosphorodithioic acids, wherein at least one metal dihydrocarbyl phosphorodithioate characterized by the general formula



wherein R¹ and R² are each independently hydrocarbyl groups containing from 3 to about 13 carbon atoms, M is a metal, and n is an integer equal to the valence of M wherein in at least one of the dihydrocarbylphosphorodithioic acids, one of the hydrocarbyl groups (D-1) is an isopropyl or secondary butyl group, the other hydrocarbyl group (D-2) contains at least 5 carbon atoms, and at least 10 mole percent of all the hydrocarbyl groups present in (D) are isopropyl groups, secondary butyl groups, or mixtures thereof.

22. The concentrate of claim 21 also containing from about 1% to about 20% by weight of (E) at least one neutral or basic alkali metal salt of a sulfonic or carboxylic acid.

- 23.** The use of the additive combination as defined in any one of claims 1 to 20 for improving oxidation stability and wear performance of lubricating oils.

Patentansprüche

1. Schmierölszusammensetzung für Verbrennungsmotoren, umfassend:

- (A) eine Hauptmenge eines Öls mit Schmierviskosität,

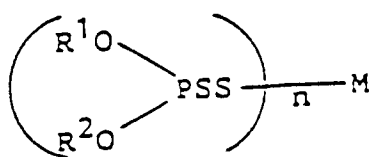
- (B) mindestens etwa 1,0 Gew.-% mindestens einer Carbonsäurederivatzusammensetzung, hergestellt durch Umsetzung von

- (B-1) mindestens einem substituierten Bernsteinsäureacylierungsmittel mit

- (B-2) mindestens einer Aminoverbindung, die in ihrer Struktur mindestens eine HN<-Gruppe enthält, wobei die substituierten Bernsteinsäureacylierungsmittel aus Substituentenresten und Bernsteinsäureresten bestehen, wobei die Substituentenreste abgeleitet sind von einem Polyalken, gekennzeichnet durch einen Mn-Wert von 1300 bis etwa 5000 und einem Mw/Mn-Verhältnis von etwa 1,5 bis etwa 4,5, wobei die Acylierungsmittel durch die Anwesenheit in ihrer Struktur von durchschnittlich mindestens 1,3 Bernsteinsäureresten pro Gewichtsäquivalent Substituentenreste gekennzeichnet sind.

- (C) mindestens eine Manganverbindung in einer Menge entsprechend 1 bis etwa 500 ppm Mangan, und

- (D) etwa 0,01 bis etwa 5 Gew.-% eines Gemisches von Metallsalzen von Dihydrocarbyldithiophosphorsäuren, wobei mindestens ein Metaldihydrocarbyldithiophosphat die allgemeine Formel (VIII) besitzt.

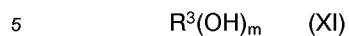


(VIII)

in der die Reste R¹ und R² jeweils unabhängig Hydrocarbylreste mit 3 bis etwa 13 Kohlenstoffatomen sind, M ein Metall ist und der Index n eine ganze Zahl ist, dessen Wert der Wertigkeit von M entspricht, wobei in mindestens einer der Dihydrocarbyldithiophosphorsäuren einer der Hydrocarbylreste (D-1) ein Isopropyl- oder sekundärer Butylrest ist, der andere Hydrocarbylrest (D-2) mindestens 5 Kohlenstoffatome enthält, und mindestens etwa 10 Mol-% von den insgesamt in (D) anwesenden Hydrocarbylresten Isopropyl-, sek.-Butylreste oder Gemische davon sind.

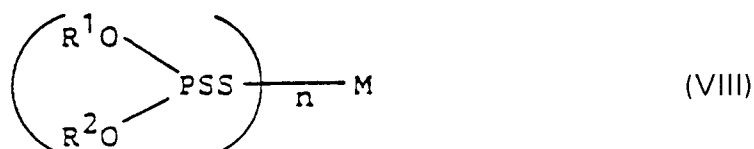
2. Schmiermittelzusammensetzung nach Anspruch 1, in der mindestens einer der Reste R¹ oder R² in (D) über ein sekundäres Kohlenstoffatom an die Sauerstoffatome gebunden ist.
3. Schmierölzusammensetzung nach Anspruch 1, in der die Manganverbindung (C) ein Salz eines sauren Materials ist, ausgewählt aus der Gruppe, bestehend aus Carbonsäuren, Sulfonsäuren und Phenolen.
4. Schmierölzusammensetzung nach Anspruch 1, in der die Manganverbindung (C) ein überbasisches Mangansalz eines Gemisches von Carbonsäuren ist.
5. Schmierölzusammensetzung nach Anspruch 1, wobei die Manganverbindung (C) in einer Menge entsprechend etwa 50 bis etwa 300 ppm Mangan vorliegt.
6. Schmierölzusammensetzung nach Anspruch 1, wobei der Wert von Mn in (B) mindestens etwa 1500 beträgt.
7. Schmierölzusammensetzung nach Anspruch 1, wobei das Verhältnis von Mw/Mn in (B) mindestens etwa 2,0 ist.
8. Schmierölzusammensetzung nach Anspruch 1, wobei in (B) etwa 0,5 Äquivalente bis zu etwa 2 Mol des Amins (B-2) pro Äquivalent Acylierungsmittel (B-1) umgesetzt wird.
9. Schmierölzusammensetzung nach Anspruch 1, wobei die Acylierungsmittel (B-1) durch die Anwesenheit in ihrer Struktur von mindestens etwa 1,5 bis etwa 2,5 Bernsteinsäureresten pro Äquivalentgewicht der Substituentenreste gekennzeichnet sind.
10. Schmierölzusammensetzung nach Anspruch 1, wobei die Manganverbindung (C) mindestens ein überbasisches Mangansalz einer Carbon- oder Sulfonsäure ist, in einer Menge entsprechend etwa 1 bis etwa 500 ppm Mangan.
11. Schmierölzusammensetzung nach Anspruch 1 oder 10, die praktisch kupferfrei ist.
12. Schmierölzusammensetzung nach Anspruch 1 oder 10, in der die Manganverbindung (C) ein überbasisches Mangancarboxylat ist.
13. Schmierölzusammensetzung nach Anspruch 1 oder 10, ebenfalls enthaltend (E) eine als Detergent wirksame Menge mindestens eines neutralen oder basischen Alkalimetallsalzes einer Sulfon- oder Carbonsäure.
14. Schmierölzusammensetzung nach Anspruch 13, wobei das Alkalimetallsalz (E) durch ein Äquivalentverhältnis von Alkalimetall zu den Äquivalenten von Sulfon- oder Carbonsäure von mindestens etwa 2:1 gekennzeichnet ist.
15. Schmierölzusammensetzung nach Anspruch 10, ebenfalls enthaltend

- (F) mindestens eine Carbonsäureesterderivatzusammensetzung, hergestellt durch Umsetzung von
 (F-1) mindestens eines substituierten Bernsteinsäureacylierungsmittels mit
 (F-2) mindestens einem Alkohol der allgemeinen Formel (XI)



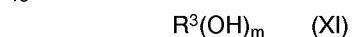
in der der Rest R^3 ein ein- oder mehrwertiger organischer Rest ist, der an die Hydroxylgruppe gebunden ist und der Index m eine ganze Zahl von 1 bis etwa 10 ist.

16. Schmierölszusammensetzung nach Anspruch 15, in der der Index m mindestens den Wert 2 hat.
17. Schmierölszusammensetzung nach Anspruch 15, wobei die durch Umsetzung des Acylierungsmittels (F-1) mit dem Alkohol (F-2) erhaltene Zusammensetzung weiter umgesetzt wird mit
 (F-3) mindestens einem Amin mit mindestens einer $>NH$ -Gruppe.
18. Schmierölszusammensetzung nach Anspruch 1, wobei die Manganverbindung (C) mindestens ein überbasisches Mangansalz mindestens einer Carbonsäure, in einer Menge entsprechend etwa 50 bis etwa 300 ppm Mangan ist, das Gemisch von Metallsalzen von Dihydrocarbyldithiophosphorsäuren (D) etwa 0,05 bis etwa 5 Gew.-% mindestens eines Metaldihydrocarbyldithiophosphats der allgemeinen Formel (VIII)



- umfaßt, in der die Reste R^1 und R^2 jeweils unabhängig Hydrocarbylreste mit 3 bis etwa 13 Kohlenstoffatomen sind, mindestens einer der Reste R^1 und R^2 über ein sekundäres Kohlenstoffatom an das Sauerstoffatom gebunden ist, M ein Metall ausgewählt aus der Gruppe bestehend aus Metallen der II. Gruppe, Aluminium, Zinn, Eisen, Cobalt, Blei, Molybdän, Mangan, Nickel oder Kupfer ist, und der Index n eine ganze Zahl ist, dessen Wert der Wertigkeit von M entspricht.

19. Schmierölszusammensetzung nach Anspruch 18, ebenfalls enthaltend
 (E) etwa 0,01 bis etwa 3 Gew.-% mindestens eines neutralen oder basischen Alkalimetallsalzes einer Sulfon- oder Carbonsäure.
20. Schmierölszusammensetzung nach Anspruch 18, ebenfalls enthaltend
 (F) etwa 0,1 bis etwa 10 Gew.-% mindestens einer Carbonsäureesterderivatzusammensetzung, hergestellt durch Umsetzung von
 (F-1) mindestens einem substituierten Bernsteinsäureacylierungsmittel mit
 (F-2) mindestens einem Alkohol der allgemeinen Formel (XI)



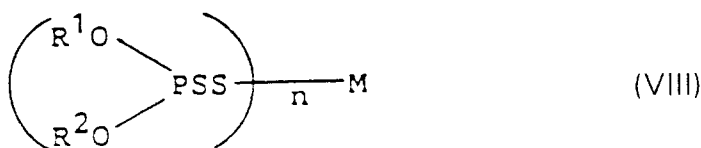
in der der Rest R^3 ein ein- oder mehrwertiger organischer Rest ist, der an die Hydroxylgruppe gebunden ist, und der Index m eine ganze Zahl von 1 bis etwa 10 ist.

21. Konzentrat zur Herstellung von Schmierölszusammensetzungen, umfassend:
 (A) etwa 20 bis etwa 90 Gew.-% eines normalerweise flüssigen, praktisch inerten organischen Verdünnungs-/Lösungsmittels,
 (B) etwa 10 bis etwa 50 Gew.-% mindestens einer Carbonsäurederivatzusammensetzung, hergestellt durch Umsetzung von
 (B-1) mindestens einem substituierten Bernsteinsäureacylierungsmittels mit
 (B-2) mindestens einer Aminoverbindung, gekennzeichnet durch die Anwesenheit von mindestens einer $HN<$ -Gruppe, wobei die substituierten Bernsteinsäureacylierungsmittel aus Substituenten-

und Bernsteinsäureresten bestehen, wobei die Substituentenreste von einem Polyalken abgeleitet sind, das durch einen Mn-Wert von 1300 bis etwa 5000 und einem Mw/Mn-Verhältnis von etwa 1,5 bis etwa 4,5 gekennzeichnet ist, die Acylierungsmittel durch die Anwesenheit in ihrer Struktur von durchschnittlich mindestens 1,3 Bernsteinsäureresten pro Äquivalentgewicht Substituentenreste gekennzeichnet sind,

(C) mindestens eine Manganverbindung in einer Menge entsprechend etwa 10 bis etwa 5000 ppm Mangan, mit der Maßgabe, daß die Manganverbindung kein neutrales Mangandihydrocarbyldithiophosphat ist, und

(D) etwa 0,05 bis etwa 15 Gew.-% eines Gemisches von Metallsalzen von Dihydrocarbyldithiophosphorsäuren, in denen mindestens ein Metaldihydrocarbyldithiophosphat durch die allgemeine Formel (VIII) gekennzeichnet ist,



in der die Reste R¹ und R² jeweils unabhängig Hydrocarbylreste mit 3 bis etwa 13 Kohlenstoffatomen sind, M ein Metall ist und der Index n eine ganze Zahl ist, dessen Wert der Wertigkeit von M entspricht, wobei in mindestens einer der Dihydrocarbyldithiophosphorsäuren einer der Hydrocarbylreste (D-1) ein Isopropyl- oder sekundärer Butylrest ist, der andere Hydrocarbylrest (D-2) mindestens 5 Kohlenstoffatome enthält, und mindestens 10 Mol-% von den insgesamt in (D) anwesenden Hydrocarbylresten Isopropyl-, sek.-Butylreste oder Gemische davon sind.

22. Konzentrat nach Anspruch 21, ebenfalls enthaltend etwa 1 bis etwa 20 Gew.-% von
(E) mindestens einem neutralen oder basischen Alkalimetallsalz einer Sulfon- oder Carbonsäure.

23. Verwendung der in einem der Ansprüche 1 bis 20 definierten Additivkombination zur Verbesserung der Oxidationsstabilität und der Verschleißigenschaften von Schmierölen.

Revendications

1. Une composition d'huile lubrifiante pour moteurs à combustion interne, qui comporte:

(A) une quantité prépondérante d'huile de viscosité lubrifiante;

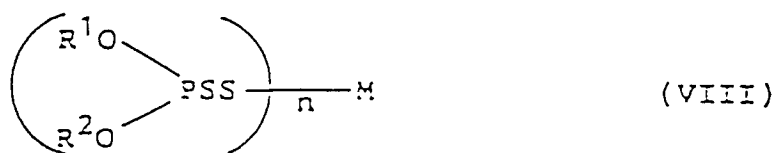
(B) au moins environ 1,0% en poids d'au moins une composition d'un dérivé carboxylique obtenu en faisant réagir

(B-1) au moins un agent acylant succinique substitué avec

(B-2) au moins un composé aminé caractérisé par la présence dans sa structure d'au moins un groupe HN<, dans lequel lesdits agents acylants succiniques substitués sont constitués de groupes substituants et de groupes succiniques dans lesquels les groupes substituants sont dérivés d'un polyalcène, ce dernier étant caractérisé par une valeur Mn de 1300 à environ 5000 et un rapport Mw/Mn d'environ 1,5 à environ 4,5, lesdits agents acylant étant caractérisés par la présence dans leur structure d'une moyenne d'au moins 1,3 groupes succiniques pour chaque équivalent pondéral de groupes substituants; et

(C) au moins un composé du manganèse dans une quantité suffisante pour obtenir de 1 à environ 500 ppm de manganèse,

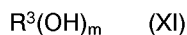
(D) d'environ 0,01% à environ 5% en poids d'un mélange de sels métalliques d'acides dihydrocarbylphosphorodithioïques dans lesquels au moins un dihydrocarbylphosphorodithioate métallique est caractérisé par la formule générale



dans laquelle R¹ et R² représentent chacun indépendamment des groupes hydrocarbyle renfermant de 3 à environ 13 atomes de carbone, M est un métal et n est un nombre entier égal à la valence de M, au moins un des acides dihydrocarbyl phosphorodithioïque, un des groupes hydrocarbyle (D-1) étant un groupe isopropyle ou un groupe butyle secondaire, tandis que l'autre groupe hydrocarbyle (D-2) renferme au moins 5 atomes de carbone, et au moins environ 10 moles pour cent de la totalité des groupes hydrocarbyle dans (D) sont des groupes isopropyle, des groupes butyle secondaire ou des mélanges de ceux-ci.

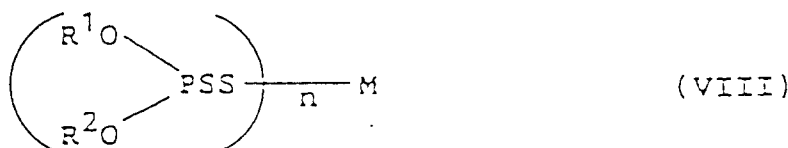
2. La composition d'huile lubrifiante de la revendication 1, dans laquelle au moins un des R¹ et R² de (D) est fixé aux atomes d'oxygène par l'intermédiaire d'un atome de carbone secondaire.
3. La composition d'huile lubrifiante de la revendication 1, dans laquelle le composé du manganèse (C) est un sel d'un produit acide choisi dans le groupe constitué des acides carboxyliques, des acides sulfoniques et des phénols.
4. La composition d'huile lubrifiante de la revendication 1, dans laquelle le composé du manganèse (C) est un sel de manganèse surbasé d'un mélange d'acides carboxyliques.
5. La composition d'huile lubrifiante de la revendication 1, renfermant d'environ 50 à environ 300 ppm de manganèse.
6. La composition d'huile lubrifiante de la revendication 1, dans laquelle la valeur de Mn dans (B) est d'au moins environ 1500.
7. La composition d'huile lubrifiante de la revendication 1, dans laquelle le rapport de Mw/Mn dans (B) est d'au moins environ 2,0.
8. La composition d'huile lubrifiante de la revendication 1, dans laquelle, dans (a), d'environ 0,5 équivalent jusqu'à environ 2 moles de l'amine (B-2) est mise à réagir par équivalent de l'agent acylant (B-1).
9. La composition d'huile lubrifiante de la revendication 1, dans laquelle les agents acylants (B-1) sont caractérisés par la présence à l'intérieur de leur structure d'au moins environ 1,5 jusqu'à environ 2,5 groupes succiniques pour chaque poids équivalent des groupes substituants.
10. La composition d'huile lubrifiante de la revendication 1, dans laquelle le composé du manganèse (C) est au moins un sel de manganèse surbasé d'un acide carboxylique ou d'un acide sulfonique en une quantité suffisante pour obtenir d'environ 1 à environ 500 ppm de manganèse.
11. La composition d'huile lubrifiante de la revendication 1 ou de la revendication 10, qui est pratiquement exempte de cuivre.
12. La composition d'huile lubrifiante de la revendication 1 ou de la revendication 10, dans laquelle le composé du manganèse (C) est un carboxylate de manganèse surbasé.
13. La composition d'huile lubrifiante de la revendication 1 ou 10, renfermant également:
(E) une quantité détergente efficace d'au moins un sel de métal alcalin, neutre ou basique, d'un acide sulfonique ou d'un acide carboxylique.
14. La composition d'huile lubrifiante de la revendication 13, dans laquelle le sel de métal alcalin (E) est caractérisé comme ayant un rapport d'équivalents de métal alcalin aux équivalents d'acide carboxylique ou d'acide sulfonique d'au moins environ 2:1.

15. La composition d'huile lubrifiante de la revendication 10, renfermant également:
(F) au moins une composition dérivée d'ester carboxylique, préparée en faisant réagir:
(F-1) au moins un agent acylant succinique substitué avec
(F-2) au moins un alcool de la formule générale



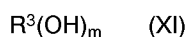
dans laquelle R^3 est un groupe organique monovalent ou polyvalent, réuni au groupe OH, et m est un nombre entier de 1 à environ 10.

16. La composition d'huile lubrifiante de la revendication 15, dans laquelle m est au moins 2.
17. La composition d'huile lubrifiante de la revendication 15, dans laquelle la composition obtenue en faisant réagir l'agent acylant (F-1) avec l'alcool (F-2) est en outre mise à réagir avec (F-3) au moins une amine renfermant au moins un groupe >NH.
18. La composition d'huile lubrifiante de la revendication 1, dans laquelle le composé du manganèse (C) est au moins un sel de manganèse surbasé d'au moins un acide carboxylique en une quantité suffisante pour obtenir d'environ 50 à environ 300 ppm de manganèse; et le mélange de sels métalliques d'acides dihydrocarbylphosphorodithioïque (D) comporte d'environ 0,05% à environ 5% en poids d'au moins un dihydrocarbylphosphorodithioate métallique caractérisé par la formule générale



dans laquelle R¹ et R² représentent chacun de façon indépendante, des groupes hydrocarbyle renferment de 3 à environ 13 atomes de carbone, au moins un des R¹ et R² est fixé à l'atome d'oxygène par l'intermédiaire d'un atome de carbone secondaire, M est un métal choisi dans le groupe constitué des métaux du groupe II, aluminium, étain, fer, cobalt, plomb, molybdène, manganèse, nickel ou cuivre, et n est un nombre entier égal à la valence de M.

19. La composition d'huile lubrifiante de la revendication 18, renfermant également:
(E) d'environ 0,01% à environ 3% en poids d'au moins un sel de métal alcalin, neutre ou basique, d'un acide sulfonique ou d'un acide carboxylique.
20. La composition d'huile lubrifiante de la revendication 18, renfermant également
(F) d'environ 0,1% à environ 10% en poids d'au moins une composition dérivée d'ester carboxylique, qui est préparée en faisant réagir
(F-1) au moins un agent acylant succinique substitué avec
(F-2) au moins un alcool de la formule générale



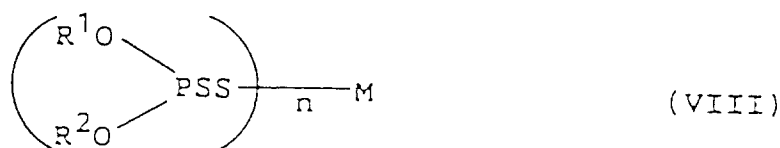
dans laquelle R^3 est un groupe organique monovalent ou polyvalent lié au groupe OH, et m est un nombre entier de 1 à environ 10.

- 21.** Un concentrat pour la formulation de compositions d'huile lubrifiante comportant:
- (A) d'environ 20% à environ 90% en poids d'un agent solvant/diluant organique, pratiquement inerte et liquide dans les conditions normales;
 - (B) d'environ 10% à environ 50% en poids d'au moins une composition d'un dérivé carboxylique obtenu en faisant réagir
 - (B-1) au moins un agent acylant succinique substitué avec
 - (B-2) au moins un composé aminé caractérisé par la présence dans sa structure d'au moins un groupe HN<, dans lequel lesdits agents acylants succiniques substitués sont constitués de

groupes substituants et de groupes succiniques dans lesquels les groupes substituants sont dérivés d'un polycalcène, ce dernier étant caractérisé par une valeur Mn de 1300 à environ 5000 et un rapport Mw/Mn d'environ 1,5 à environ 4,5, lesdits agents acylant étant caractérisés par la présence dans leur structure d'une moyenne d'au moins 1,3 groupes succiniques pour chaque équivalent pondéral de groupes substituants; et

(C) au moins un composé du manganèse dans une quantité suffisante pour obtenir d'environ 10 à environ 5000 ppm de manganèse, sous la condition que le composé du manganèse n'est pas un dihydrocarbylphosphorodithioate de manganèse neutre; et

(D) d'environ 0,05% à environ 15% en poids d'un mélange de sels métalliques d'acides dihydrocarbylphosphorodithioïques dans lesquels au moins un dihydrocarbylphosphorodithioate métallique est caractérisé par la formule



dans laquelle R¹ et R² représentent chacun indépendamment des groupes hydrocarbyle renfermant de 3 à environ 13 atomes de carbone, M est un métal et n est un nombre entier égal à la valence de M, au moins un des acides dihydrocarbyl phosphorodithioïque, un des groupes hydrocarbyle (D-1) étant un groupe isopropyle ou un groupe butyle secondaire, tandis que l'autre groupe hydrocarbyle (D-2) renferme au moins 5 atomes de carbone, et au moins 10 moles pour cent de la totalité des groupes hydrocarbyle dans (D) sont des groupes isopropyle, des groupes butyle secondaire ou des mélanges de ceux-ci.

22. Le concentré de la revendication 21, qui renferme également d'environ 1% à environ 20% en poids de:
(E) au moins un sel de métal alcalin, neutre ou basique, d'un acide sulfonique ou carboxylique.

23. Utilisation de la combinaison additive tel que définie dans l'une quelconque des revendications 1 à 20, pour améliorer la stabilité à l'oxydation et le comportement à l'usure des huiles lubrifiantes.