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(54) Synergistic combination of additives useful in power transmitting compositions.

(57) A mutually compatible combination of additives and their use to impart anti-wear, dispersancy and friction modification to power transmission compositions, particularly automatic transmission fluids, is disclosed. The additives comprise organic phosphite ester such as dioleyl monohydrogenphosphite; hydroxyl amine compound, such N-octadecyl diethanolamine, N-octadecyloxypropyldiethanol amine, or N-octadecylthiopropyl diethanolmine, and dispersant such as that derived by reacting a polyisobutenyl succinimide with a phosphosulfurized terpene, either alone or in combination with a borated, aminated dispersant such as that derived by reacting a polyisobutenyl succinimide with boric acid.

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Description

SYNERGISTIC COMBINATION OF ADDITIVES USEFUL IN POWER TRANSMITTING COMPOSITIONS

The present invention relates to a synergistic mixture of hydrocarbon soluble or dispersible additives for oleaginous compositions such as lubricating oils, including power transmitting fluids and engine lubricating oils, and to the oleaginous compositions in which they are contained.

There are many instances, as is well known, particularly under boundary lubrication conditions where two moving surfaces in contact with each other must be lubricated, or otherwise protected, so as to prevent wear, and to insure continued movement. There are other instances where friction between two rubbing surfaces is sought to be modified but not necessarily minimized. By controlling friction between two surfaces, the power required to impart movement from one surface to another is also controlled.

For example, a specialized property sought to be imparted to certain lube oil compositions adapted for use as an automatic transmission fluid is the friction modification characteristic of the fluid. This property distinguishes automatic transmission fluids (ATF) from other lubricants, and in fact between types of ATF as well. Such characteristic quality has received the most attention by both the transmission manufacturers and fluid producers for many years. This attention stems from the fact that the friction requirements of an ATF are unique and depend on the transmission and clutch design, as well as on the type of clutch plate material used.

Another property sought to be imparted to lubricating oil compositions including automatic transmission fluids is reduced wear such as bearing and power component wear.

As is also well known, both wear and friction modification can be controlled through the addition of suitable additives with varying degrees of success.

While there are many known additives which may be classified as anti-wear, or friction modifying agents, it is also known that many of these additives act in a different physical or chemical manner and often compete with one another, e.g. they may compete for the surface of the moving metal parts which are subjected to lubrication. Accordingly, extreme care must be exercised in the selection of these additives to insure compatibility and effectiveness.

The metal dihydrocarbyl dithiophosphates are one of the additives which are known to exhibit anti-oxidant and anti-wear properties. The most commonly used additives of this class are the zinc dialkyl dithiophosphates (ZDDP) which are conventionally used in lubricant compositions. While such zinc compounds afford excellent oxidation resistance and exhibit superior anti-wear properties, they can be corrosive.

Both anti-wear and friction modifying agents function by forming a coating on the surface of the moving metal parts. The coating bonds are generally effected physically and/or chemically. Consequently, if the bonding between the anti-wear agent and the metal part is stronger than the bonding between the friction modifying agent and the metal part, the anti-wear agent will displace the friction modifying agent at the metal surface, i.e. at the metal/fluid lubrication boundary interface. This results in a loss in the ability of the friction modifying agent to exert its intended effect.

Various tests have been designed by auto manufacturers for measuring ATE friction and anti-wear properties which if passed are indicative of the fact that such properties will match the requirements of particular transmission designs and result in transmission durability and smooth shifting under a variety of load conditions.

Friction modification is typically evaluated on an SAE No. 2 friction apparatus. In this test, the motor and flywheel of the friction machine (filled with fluid to be tested) are accelerated to constant speed, the motor is shut off and the flywheel speed is decreased to zero by application of the clutch. The clutch plates are then released, the flywheel is again accelerated to constant speed, and the clutch pack which is immersed in the test fluid is engaged again. This process is repeated many times with each clutch engagement being called a cycle.

During the clutch application, friction torque is recorded as a function of time. The friction data obtained are either the torque traces themselves or friction coefficients calculated from the torque traces. The shape of the torque trace desired is set by the auto manufacturers. One way of expressing this shape mathematically is to determine the torque: (a) when the flywheel speed is midway between the maximum constant speed selected and zero speed (such torque measurement is referred to herein as T_D) and (b) when the flywheel speed approaches zero rpm (such torque measurement is referred to herein as T_0). Such torques can then be used to determine the torque ratio which is expressed as T_0/T_D, or alternatively, to determine the torque differential T_0-T_D. The optimum target values for torque ratio and torque differential are set by the auto manufacturers. As the T_0/T_D increasingly exceeds 1, a transmission will typically exhibit shorter harsher shifts as it changes gears. On the other hand as T_0/T_D decreases below 1, there is an increasingly greater danger of clutch slippage when the transmission changes gears. Similar relationships exist with respect to a T_0-T_D target value of 0.

While many automatic transmission fluids can achieve target values of T_0/T_D after a minimum number of cycles, it becomes increasingly more difficult to sustain such target values as the number of cycles are increased. The ability of an ATF to sustain such desired friction properties is referred to herein as friction stability. A high level of friction stability is difficult to achieve with ATF's which contain certain anti-wear agents. It is believed that as the ATF ages under the influence of the heat of friction, the anti-wear agent can break down and the decomposition products displace conventional friction modifiers at the metal/fluid lubrication boundary interface. As a result, the fluid may exhibit varying friction properties.

Attempts to improve of friction stability by simply adding more friction modifier have not met with success because this tends to reduce the breakaway static torque (T_S) of the fluid. This parameter when expressed as the breakaway static torque ratio (T_S/T_D) reflects the relative tendency of engaged parts, such as clutch packs, bands and drums, to slip under load. If this value is too low, the slippage can impair the driveability and safety of the vehicle.

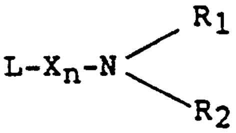
Transmission designs have undergone radical changes, thereby necessitating the formulation of ATF additives capable of meeting new and more stringent property requirements needed to match such design changes.

No base oil alone can even approach the many special properties required for ATF service. Consequently, it is necessary to employ several chemical additives, each of which is designed to impart or improve a specific property of the fluid. Consequently, it becomes particularly advantageous when one additive can perform more than one function, thereby reducing the number of additives needed to be present in the formulation.

Accordingly, there has been a continuing search for new additives possessed of one or more properties which render them suitable for use in ATF compositions, as well as other oleaginous compositions. There also has been a search for new combinations of additives which not only provide ATF compositions, as well as other oleaginous compositions, with the various specific properties that are required, but which are compatible with each other in the sense that they do not exhibit any substantial tendency to compete with each other, nor to otherwise reduce the effectiveness of the various additives in the compositions. The present invention was developed in response to this search.

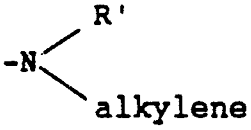
U.S. Patent 2,290,880 discloses ethers of alcohol amines which may be used as interface modifying agents in a wide variety of arts. The compounds are said to be useful in lubricating oils and the like, thus enabling the production of effective boring oils, cutting oils, drilling oils, wire drawing oils, extreme pressure lubricants and the like.

U.S. Patent 3,034,907 discloses agents which are effective for hindering or retarding rust formation on iron surfaces and ice formation in the intake system of internal combustion engines. The agents which are disclosed are characterized by a content of (a) a hydrophobic organic carrier, (b) a carboxylic acid amide monocarboxylic acid, and (c) an at least equivalent amount of a hydroxyalkylated nitrogen base which contains at least one lipophilic radical. The hydroxyalkylated nitrogen base corresponds to the general formula:



$$L{-}X_n{-}N\begin{matrix} R_1 \\ R_2 \end{matrix}$$

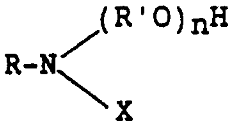
wherein L represents a lipophilic radical; X represents a bridging member which is bound to the nitrogen atom by means of an aliphatic carbon atom and which is selected from lower -O-alkylene, -S-alkylene, -O-hydroxyalkylene, -S-hydroxyalkylene,



$$-N\begin{matrix} R' \\ \text{alkylene} \end{matrix}$$

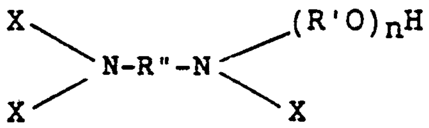
(R' = H, alkyl, hydroxyalkyl), -CO-O-alkylene, and -CO-O-hydroxyalkylene radicals; n represents the integer 0 or 1; R_1 represents hydrogen, a lower alkyl or lower hydroxyalkyl or lower aminoalkyl radical; and R_2 is the same as (L-X_n) and R_1. In one embodiment, L represents an aliphatic C_{12}-C_{18} hydrocarbon radical, n is 0, and at least one of R_1 and R_2 is a low molecular weight hydroxyalkyl or hydroxyalkylaminoethyl radical.

U.S. patent 3,235,501 discloses foam-inhibited oil compositions which comprise a oleaginous material, a detergent additive, a silicone anti-foamant, and a small amount of a polyalkyl oxylated aliphatic amine which conforms to one of the following formulas depending on whether the amine from which they are prepared is a mono- or diamine:



$$R{-}N\begin{matrix} (R'O)_nH \\ X \end{matrix} \qquad (1)$$

where R is an aliphatic radical of from about 4 to about 24 carbon atoms, R′O is an alkylene oxide radical selected from the group consisting of the ethylene oxide and propylene oxide radicals, n is an integer from 1 to about 25 and X is selected from hydrogen, R and $(R'O)_nH$ radicals, the total value of n is in any instance being no greater than 25 and



(2)

where R″ is an aliphatic radical having from 2 to about 6 carbon atoms, R′O, n and X are defined in formula 1 but at least one X is an R radical and the total value of n in any instance being no greater than about 25.

U.S. Patent 3,255,253 discloses amine-containing polyols which are prepared by first cyanoethylating an alcohol in the presence of a basic catalyst. The cyanoethylated alcohol is then hydrogenated to produce a primary amine, whereafter the primary amine is reacted with an alkylene oxide in the presence of a basic catalyst to form the desired amine-containing polyol. The amine-containing polyols are said to be useful for preparing polyurethane products, as hardeners for polyepoxide resins, and in the preparation of coatings and plasticizers.

U.S. Patent 3,456,012 relates to polyolefin adducts of gamma-alkoxypropylamines having surfactant properties.

U.S. Patent 3,464,925 relates to hydraulic fluids which contain certain aminotriols. The aminotriols are obtained by heating propylene oxide and triisopropylamine under pressure, in the presence of an alkaline catalyst.

U.S. Patent 3,705,139 discloses alkyl sulfide compounds of the formula:

R_1-S-R_2-A-$(R_3O)_nZ$,

where R_1 represents a hydrocarbyl radical having 6 to 22 carbon atoms, R_2 and R_3 each represents a hydrocarbyl radical having 1 to 4 carbon atoms, A can represent nitrogen, n represents an integer in the range of 0-100, and Z can represent hydrogen. The alkyl sulfide compounds are disclosed as being antistatic agents.

U.S. Patent 3,933,659 discloses lubricating oil compositions which comprise a major amount of an oil of lubricating viscosity, and an effective amount of each of the following: (1) an alkenyl succinimide, (2) a Group II metal salt of a dihydrocarbyl dithiophosphoric acid, (3) a compound selected from the group consisting of (a) fatty acid esters of dihydric and other polyhydric alcohols, and oil soluble oxyalkylated derivatives therof, (b) fatty acid amides of low molecular weight amino acids, (c) N-fatty alkyl-N,-N diethanol amines, (d) N-fatty alkyl-N,N-di(ethoxy-ethanol) amines, (e) N-fatty alkyl-N,N-di-poly(ethoxy) ethanol amines, and (f) mixtures thereof, and (4) a basic sulfurized alkaline earth metal alkyl phenate. Such lubricating compositions are useful as functional fluids in systems requiring fluid coupling, hydraulic fluid and/or lubrication of relatively moving parts, particularly as automatic transmission fluids.

U.S. Patent 4,010,106 discloses lubricating oil compositions which comprise an oil of lubricating viscosity, and an effective amount of each of the following: (1) an alkenyl succinimide, (2) a Group II metal salt of a dihydrocarbyl dithiophosphoric acid, (3) a frictional modifier, (4) a basic sulfurized alkaline earth metal alkyl phenate, and (5) a chlorinated olefin containing from about 15 to 50 carbon atoms, from 20 to 60% by weight chlorine, and having a boiling point of at least about 300°F. Such lubricating compositions are useful as functional fluids in systems requiring fluid coupling, hydraulic fluid and/or lubrication of relatively moving parts, particularly as automatic transmission fluids.

U.S. Patent 4,201,684 relates to lubricating oil compositions adapted for use as a crankcase lubricant in internal combustion engines containing a friction reducing amount of a sulfurized fatty acid amide, ester or ester-amide of an oxyalkylated amine.

U.S. Patent 4,231,883 relates to the use of an alkoxylated hydrocarbyl amine in a lubricating oil or fuel to reduce the friction of an internal combustion engine in which the lubricating oil or fuel is used. An example of the alkoxylated hydrocarbyl amine compounds that are disclosed in this patent is N-N-bis(2-hydroxyethyl) oleylamine.

U.S. Patent 4,486,324 discloses an aqueous hydraulic fluid comprising at least 80% water and containing a hydrocarbyl-substituted succinic acid, a zinc dihydrocarbyl dithiophosphate, a hydroxyalkylamine, sodium alkyl benzene sulfonate, and optionally, a polyalkylene glycol mono-fatty acid ester.

U.S. Patent 4,650,865 relates to a process for preparing tertiary ether amines which exhibit surface active properties. The tertiary ether amines may be used as surfactants and as starting materials for the production of surface-active derivatives, such as for example, amineoxides and quaternary ammonium compounds.

U.S. Patent 4,129,508 relates to lubricant and fuel compositions characterized by improved demulsifying properties. The patent discloses an automatic transmission fluid which includes a number of additives including a dialkyl phosphite, the reaction product of a polyisobutenyl-substituted succinic anhydride, commercial tetraethylene pentamine, and boric acid prepared as set forth in U.S. Patent 3,254,025, and a conventional friction modifier based on polyoxyethylene tallow amine (Ethomeen T/12), the reaction product of polyisobutenyl succinic anhydride and an ethylene polyamine, and Ethomeen C/15. The Ethomeen compounds are available commercially from the Armak Chemical Division of Akzo Chemie.

U.S. Patent 2,151,300 relates to lubricating oil compositions which contain a major proportion of a mineral lubricating oil, a minor proportion of an organic phosphite, and a small amount, sufficient to bring about substantial stability of the phosphorous compound, of an oil-soluble organic amine.

U.S. Patent 4,634,543 relates to a fluid composition for use in a shock absorber. The fluid composition comprises a lubricating base oil, a boron- containing compound, and a phosphoric acid ester and/or phosphorous acid ester, such as dioleyl hydrogenphosphite.

U.S. Patent 3,645,886 relates to the concept of reducing or preventing the fouling of process equipment in petroleum or chemical industries wherein an organic feed stock is subjected to heat exchange at a temperature of from about 200° to about 1300°F, and there is added to that organic feed stock a mixture of a fatty acid ester of an alkanol amine and a mono-, di-, or triorganic phosphite ester.

U.S. Patent 3,484,375 relates to the production of additives for lubricating oils, middle distillate fuels, residual fuels or reduced crudes in order to improve their resistance to oxidation, sludge formation, to improve their viscosity index, or to improve their flowability and pour point characteristics. The additives are prepared by reacting an organic phosphite ester containing at least one hydroxyl group attached to the phosphorous with alkaline polyamines or aminoalcohols.

U.S. Patent 4,170,560 discloses additive compositions for use in crank case lubricating oils comprising a mixture of an oil soluble anti-oxidant and a oil soluble hydroxylamine which includes both Ethomeens and Ethoduomeens, which are trade names for compounds available commercially from the Armak Chemical Division of Akzo Chemie.

U.S. Patent 4,529,528 discloses the reaction product of, for example, an Ethomeen, a dialkyl phosphite and a boron compound.

U.S. Patent 4,382,006 discloses lubricating composition containing a friction reducing additive comprised of ethoxylated amines, which include Ethomeen, and borated derivates thereof.

U.S. Patent 2,917,160 discloses the use of certain hydroxylated tertiary amines which include Ethomeen, as a corrosion inhibiting surface active lubricant for metal working. The amines may be used in the form of a salt. Phosphoric acid salts are illustrated.

U.S. Patent 3,186,946 discloses cutting fluids in which the active lubricating component is a borate salt of a tertiary amine which includes both Ethomeen and Ethoduomeens.

U.S. Patent 4,557,845 discloses the reaction product of an Ethomeen and a di-(C_1-C_6 hydrocarbyl) phosphite. The reaction product is formed at a temperature between about 80 and 280°C and in reactant proportions such that from about 5 to 100% of the amine hydroxy groups are reacted with the phosphite.

U.S. Patent 3,509,052 relates to lubricating compositions containing a lubricating oil, a dispersant which is a derivative of a substituted succinic acid, and a demulsifier. The demulsifier may comprise, for example, an Ethomeen, but the preferred demulsifiers are polyoxyalkylene, polyols and derivatives thereof.

U.S. Patent 3,502,677 relates to substituted polyamines which are useful as additives in lubricating compositions, fuels, hydrocarbon oils and power transmitting fluids. The substituted polyamines are prepared by reacting an alkylene polyamine with a substantially hydrocarbon-substituted succinic acid-producing compound and a phosphorous acid-producing compound. Other nitrogen- and phosphorous-containing succinic derivatives are disclosed in U.S. Patent 3,513,093. The products disclosed in that patent are also useful as additives in lubricating oils, fuels, plastics, etc.

U.S. Patent 3,394,179 discloses an oil soluble lubricant additive which is the reaction product of a phosphosulfurized hydrocarbon and an amide which is formed by reacting an aliphatic polyamine with a high molecular weight monocarboxylic acid. The phosphosulfurized hydrocarbon is prepared by reacting a terpene, a petroleum fraction or a polymer of a C_2-C_6 olefin with a sulfide of phosphorous.

U.S. Patent 2,316,078 discloses lubricating oil compositions which include the reaction product obtained by reacting a phosphorous sulfide, such as P_2S_5, with polymers of olefinic hydrocarbons, particularly low molecular weight monoolefinic hydrocarbons.

U.S. Patent 2,805,217, relates to condensation products of terpenes with phosphorous sesquisulfide and oxygen. The condensation products are employed in lubricating oil compositions as antioxidants and detergents.

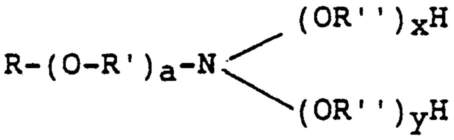
U.S. Patent 2,875,188 relates to phosphosulfurized hydrocarbons which are used as additives to impart detergency, extreme pressure, and other properties to lubricants. The hydrocarbons which are subjected to phosphosulfurization in accordance with this patent include, for example, C_2-C_{10} monoolefinic polymers having a molecular weight in the range of 500-100,000 and petroleum bright stocks boiling above 700°F.

U.S. Patent 3,511,780 relates to an additive that is useful as a sludge dispersant, anti-wear agent, anti-oxidant and inhibitor of harmful deposit formation in hydrocarbon compositions including fuel oils and lubricants. The additive is prepared by condensing an alkenyl succinic anhydride with an aliphatic polyamine or with an aliphatic polyamine and a carboxylic acid, followed by further reaction of the condensation product with a phosphosulfurized hydrocarbon and with a dialkyl dithiophosphoric acid. A suitable phosphosulfurized hydrocarbon is exemplified by P_2S_5-treated polyisobutylene.

U.S. Patent 3,850,822 discloses a lubricating oil for an internal combustion engine comprising a major portion of oil and a minor portion of an additive package which includes a dispersant, a phosphosulfurized olefinic hydrocarbon, and a phosphorothionyl disulfide of phenol or of a C_1-C_{18} alkyl phenol. In one embodiment, the dispersant is made by the reaction of a polyisobutenyl succinic anhydride with a tetraethylene pentamine, the phosphosulfurized olefinic hydrocarbon is made from the reaction of P_2S_5 with alpha-pinene, and the phosphorothionyl disulfide is that of a nonyl phenol.

U.S. Patent 4,557,845 discloses that the products of reaction between a 2-hydroxethyl alkylamine or certain higher oxylated members, and a dihydrocarbyl phosphite compound are effective friction modifiers and fuel reducing additives for internal combustion engines when such products are compounded with lubricants and liquid fuels. A similar disclosure is contained in U.S. Patent 4,529,528, except that the products are prepared by reacting a bis(2-hydroethyl)alkylamine, a dihydrocarbyl phosphite and a boron compound.

U.S. Patent 4,704,217 discloses a gasoline crankcase lubricant which contains a dialkoxylated alkyl polyoxyalkyl amine friction modifier having the formula:



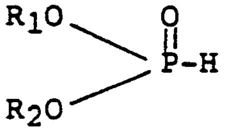
$$R-(O-R')_a-N\begin{array}{l}(OR'')_xH\\ (OR'')_yH\end{array}$$

wherein R is a C_1-C_{20} hydrocarbyl radical, R′ and R″ are divalent C_1-C_{10} alkylene groups, a is an integer of about 1 to about 10 and x+y has a value of about 1 to 20.

SUMMARY OF THE INVENTION

The present invention is based in part on the discovery that a synergistic combination of compounds possess multifunctional properties including those of anti-wear, friction modification and friction durability. In addition the individual compounds comprising such combination are compatible with each other, are stable, and hence do not necessarily adversely affect friction stability of automatic transmission fluids. In short, the combination of the individual compounds is considered to be a desirable combination of additives for use in powder transmission fluids, and more particularly in automatic transmission fluids.

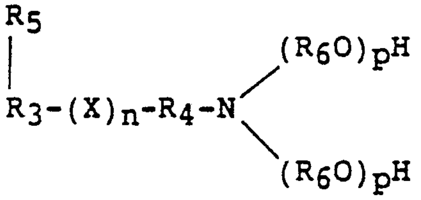
In one aspect of the present invention, an organic phosphite ester having the formula:



$$\begin{array}{l}R_1O\\ R_2O\end{array}\!\!>\overset{O}{\overset{\|}{P}}-H \qquad I$$

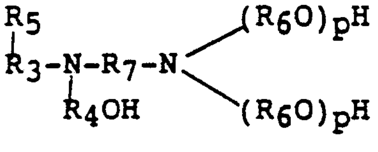
wherein R_1 and R_2, independently, represent the same or different C_{12}-C_{24} saturated or unsaturated, straight or branched chain hydrocarbyl radical having at most two unsaturated linkages is employed in a 3-component combination of additives which further includes a hydroxyl amine compound friction modifier and a dispersant material.

The hydroxyl amine compound is characterized by one of the following formulas II or III



$$\overset{R_5}{\overset{|}{R_3}}-(X)_n-R_4-N\begin{array}{l}(R_6O)_pH\\ (R_6O)_pH\end{array} \qquad II$$

wherein R_3 represents a C_3-C_{27} saturated or unsaturated aliphatic hydrocarbon radical; R_4 represents a straight or branched chain C_1-C_6 alkylene radical; R_5 represents H or CH_3, R_6 represents a straight or branched chain C_2-C_5 alkylene radical; p, independently, represents 1-4; X represents O or S; and n represents 0 or 1; and wherein it is preferred that there are a total of from about 18 to about 30 carbon atoms in the compound; or



$$\overset{R_5}{\overset{|}{R_3}}-\underset{\underset{R_4OH}{|}}{N}-R_7-N\begin{array}{l}(R_6O)_pH\\ (R_6O)_pH\end{array} \qquad III$$

wherein R_3, R_4, R_5, R_6 and p are the same as for formula II above, wherein R_7 represents a straight or branched chain C_1-C_5 alkylene radical, and wherein it is preferred that there are a total of from about 18 to about 30 carbon atoms in the compound.

The dispersant materials contemplated for use in this invention are phosphosulfurized detergent/dispersant materials, either alone or, more preferably, in combination with a borated, aminated, long chain hydrocarbyl-substituted dicarboxylic material.

The phosphosulfurized dispersant/detergent materials, which are described more fully hereinafter, may comprise, for example, an oil soluble product formed by reacting a hydrocarbyl-substituted dicarboxylic acid material with a polyamine or with a polyamine and carboxylic acid to form an imide condensation product, followed by further reaction of the imide condensation product with an organic thioacid of phosphorous.

The borated, aminated, long chain hydrocarbyl-substituted dicarboxylic acid material, which are described more fully hereinafter, may comprise, for example, the product formed by reacting a boron compound, such as boric oxide and metaborate, boric acid, or a mono-, di-, and trialkyl borate with an oil soluble product formed by reacting a hydrocarbyl-substituted dicarboxylic acid material with a polyamine or with a polyamine and carboxylic acid to form an imide condensation product.

The above combination of additives is particularly suited to meeting the stringent ATF requirements from the standpoint of the proper balance of anti-wear, static and dynamic friction coefficients, friction modification and stability, dispersancy, sludge inhibition, anti-oxidation and corrosion resistance properties.

In another aspect of the invention, the above-described organic phosphites may be employed in combination with the phosphosulfurized material and the reaction product of the hydroxyl amine compound with a boron compound such as boric acid or a C_1-C_4 trialkyl borate.

In another aspect of the present invention, there is provided a lubricating oil composition adaptable for use as a power transmitting fluid comprising the above-described 3-component combination of additives.

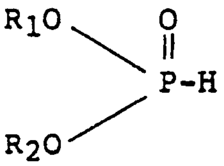
In a still further embodiment of the present invention, there is provided a lubricating oil composition concentrate adaptable for use as an automatic transmission fluid comprising the above-described 3-component combination of additives.

In another embodiment of the present invention, there is provided a lubricating oil composition concentrate adaptable for use as a power transmitting fluid which comprises a lubricating oil having dissolved or dispersed therein at least one of the herein-described organic phosphite compounds, at least one of the herein-described hydroxyl amine compounds, and at least one of the herein-described phosphosulfurized materials, preferably in combination with one of the herein-described borated, aminated long chain hydrocarbyl-substituted dicarboxylic acid materials.

In another embodiment of the present invention there is provided a process for improving the static and dynamic friction coefficients and the frictional stability properties of a lubricating oil composition which is adapted for use as a power transmitting fluid which comprises adding to said lubricating oil composition at least one of the organic phosphite compounds, at least one of the hydroxyl amine compounds, and at least one of the phosphosulfurized materials disclosed herein.

Description Of Preferred Embodiments

The organic phosphite ester additives of the present invention can be represented by the structural formula:



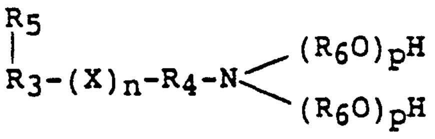
$$(R_1O)(R_2O)\overset{O}{\overset{\|}{P}}-H \qquad I$$

where R_1, and R_2 which may be the same or different independently can represent an alkyl radical (preferably straight chain alkyl), typically about C_6 to about C_{30}, preferably about C_{10} to about C_{26}, and most preferably about C_{12} to about C_{24} alkyl, or an alkenyl radical (preferably straight chain alkenyl), typically about C_6 to about C_{30}, preferably about C_{10} to about C_{26}, and most preferably about C_{12} to about C_{24} alkenyl. When R_1 and/or R_2 is an alkenyl radical, it is preferable that there be no more than two unsaturated linkages in the radical.

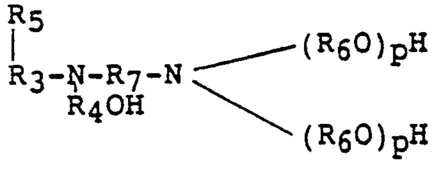
Representative examples of suitable R_1 and R_2 groups of formula (I) include hexyl, heptyl, octyl, 2-ethylhexyl, isooctyl, tertiary-octyl, nonyl, isononyl, tertiary-nonyl, secondary-nonyl, decyl, isodecyl, undecyl, dodecyl, tridecyl, palmityl, stearyl, isostearyl, octenyl, nonenyl, decenyl, dodecenyl, oleyl, linoleyl and linolenyl.

The more preferred R_1 and R_2 groups include n-octadecyl, n-hexadecyl, n-dodecyl, n-tetradecyl, oleyl and stearyl. In most cases it is preferred that R_1 and R_2 are the same for any given organic phosphite ester. The most preferred phosphite is dioleyl monohydrogen phosphite. The organic phosphites can be obtained by the direct esterification of phosphorous acid or a phosphorous trihalide with an alcohol or a mixture of alcohols. The methods for preparing the organic phosphite esters are known in the art and are discussed, for example, in U.S. Patent 3,513,093, the disclosure of which is incorporated herein by reference.

The hydroxyl amine compounds contemplated for use in this invention are characterized by one of the following formulas II and III:



$$\overset{R_5}{\overset{|}{R_3}}-(X)_n-R_4-N\begin{matrix}(R_6O)_pH\\(R_6O)_pH\end{matrix} \qquad II$$

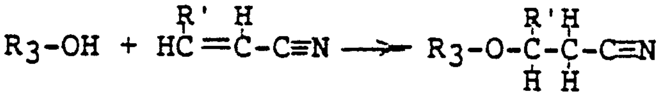


$$\overset{R_5}{\overset{|}{R_3}}-\underset{R_4OH}{N}-R_7-N\begin{matrix}(R_6O)_pH\\(R_6O)_pH\end{matrix} \qquad III$$

where R_3 represents a straight or branched chain, saturated or unsaturated, aliphatic hydrocarbon radical (preferably straight chain alkylene), typically about C_3 to about C_{27}, preferably about C_{10} to about C_{20}, and most preferably about C_{16} to C_{18} alkylene; R_4 represents a straight or branched chain alkylene radical (preferably straight alkylene), typically C_1 to about C_6, preferably about C_2 to about C_4, and most preferably C_3 alkylene; R_5 represents H or CH_3, preferably H; R_6, independently, represents a straight or branched chain alkylene radical (preferably straight chain alkylene) typically about C_2 to about C_5, and preferably C_2 alkylene, R_7 represents a straight or branched chain C_1-C_5 alkylene radical (preferably C_2 alkylene), independently, is 1-4, preferably 1-3 (e.g., 1); X represents O or S, preferably O; and n represents 0 or 1. In a particularly preferred embodiment, the hydroxylamine would be characterized by the formula II wherein X represents O, R_3 and R_5 contain a combined total of 18 carbon atoms, R_4 represents C_3 alkylene, R_6 represents C_2 alkylene, and p is 1. In all cases, it is preferred that the hydroxyl amine compounds contain a combined total of from about 18 to about 30 carbon atoms.

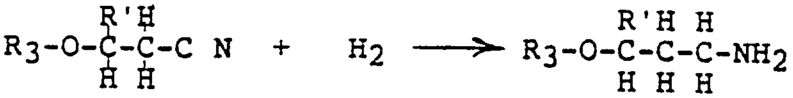
When the hydroxyl amine compounds are characterized by the formula II and when X is O and n is 1, the hydroxyl amine compounds can be prepared, for example, by a multi-step process wherein an alkanol is first reacted, in the presence of a catalyst, with an unsaturated nitrile such as acrylonitrile to form an ether nitrile intermediate. The intermediate is then hydrogenated, preferably in the presence of a conventional hydrogenation catalyst such as Raney nickle to form an ether amine. The ether amine is then reacted with an alkylene oxide, such as ethylene oxide in the presence of an alkaline catalyst by a conventional method at a temperature in the range of about 90 - 150°C. The overall process for preparing the desired hydroxyl amine compounds can be illustrated by the following equations:

EQ. 1



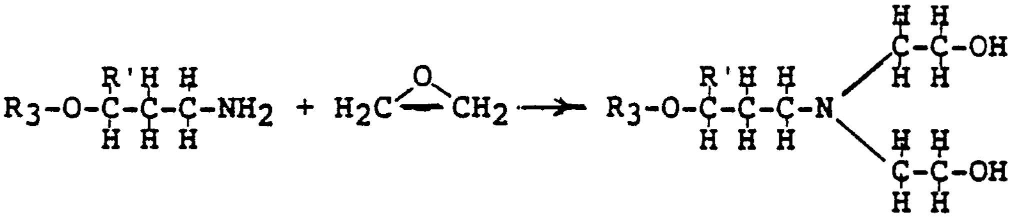
$$R_3\text{-OH} + H\overset{R'}{C}=\overset{H}{C}\text{-}C\equiv N \longrightarrow R_3\text{-O-}\underset{H}{\overset{R'}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}C\equiv N$$

EQ. 2



$$R_3\text{-O-}\underset{H}{\overset{R'}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}C\ N + H_2 \longrightarrow R_3\text{-O-}\underset{H}{\overset{R'}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}NH_2$$

EQ. 3



$$R_3\text{-O-}\underset{H}{\overset{R'}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}NH_2 + H_2C\overset{O}{\frown}CH_2 \longrightarrow R_3\text{-O-}\underset{H}{\overset{R'}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}N\begin{matrix}\diagup\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-OH}\\ \diagdown\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-OH}\end{matrix}$$

where R_3 represents straight or branched chain alkyl as described above and R′ represents hydrogen or a C_1 to C_3 alkyl substituent on the alkylene radical constituting R_4 in formula II.

Another method of preparing the present hydroxyl amine compounds, when X is O and n is 1, is by reacting a fatty acid with ammonia or an alkanol amine, such as ethanolamine, to form an intermediate which can be further oxyalkylated by reaction with an alkylene oxide, such as ethylene oxide or propylene oxide. A process of this type is discussed, for example, in U.S. Patent 4,201,684, the disclosure of which is incorporated herein by reference.

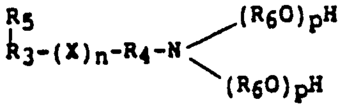
When X is S and n is 1, the hydroxyl amine friction modifying compounds can be formed, for example, by effecting a conventional free radical reaction between a long chain alpha-olefin with a hydroxyalkyl mercaptan, such as beta-hydroxyethyl mercaptan, to produce a long chain alkyl hydroxyalkyl sulfide. The long chain alkyl hydroxyalkyl sulfide is then mixed with thionyl chloride at a low temperature and thereafter heated to about 40°C to form a long chain alkyl chloroalkyl sulfide. The long chain alkyl chloroalkyl sulfide is then caused to react with a dialkanol amine, such as diethanolamine, and, if desired, with an alkylene oxide, such as ethylene oxide, in the presence of an alkaline catalyst and at a temperature on the order of about 100°C to form the desired hydroxyl amine compounds. Processes of the above type are known in the art and are discussed, for example, in U.S. Patent 3,705,139, the disclosure of which is incorporated herein by reference.

In cases where n is 0, the present hydroxyl amine friction modifiers are well known in the art and are described, for example, in U.S. Patents 3,186,946, 4,170,560, 4,231,883, 4,409,000 and 3,711,406, the disclosures of these patents being incorporated herein by reference. Such hydroxyl amine oompounds are available commercially, from the Armak Chemical Division of Akzo Chemie, for example, under the trade names Ethomeen, Ethomeen T/12, Ethomeen C/15, Ethoduomeen T/12, Ethoduomeen T/15, etc.

Representative examples of suitable compounds falling within the scope of the above structural formulas II and III are provided below in Tables 1 and 2 in chart form wherein each of the variable groups are associated in specific compounds.

Table 1

FORMULA:



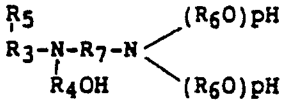
$$\overset{R_5}{R_3}\text{-}(X)_n\text{-}R_4\text{-}N\begin{cases}(R_6O)_pH\\(R_6O)_pH\end{cases}$$

II

R_5	R_3	X	n	R_4	R_6	p
H-	$-C_3H_6-$	-	0	$-CH_2-$	$-C_2H_4-$	1
CH_3-	$-C_4H_8-$	-	0	$-C_4H_8-$	$-C_3H_6-$	2
H-	$-C_5H_{10}-$	-	0	$-C_2H_4-$	$-C_4H_8-$	3
CH_3-	$-C_6H_{12}-$	-	0	$-C_2H_4-$	$-C_5H_{10}-$	4
H-	$-C_{27}H_{54}-$	-	0	$-C_3H_6-$	$-C_2H_4-$	3
CH_3-	$-C_{10}H_{20}-$	-	0	$-C_6H_{12}-$	$-C_2H_4-$	2
H-	$-C_{20}H_{40}-$	-	0	$-C_3H_6-$	$-C_2H_4-$	2
H-	$-C_{16}H_{32}-$	-	0	$-C_3H_6-$	$-C_2H_4-$	2
CH_3-	$-C_{17}H_{34}-$	-	0	$-C_3H_6-$	$-C_2H_4-$	2
H-	$-C_{18}H_{36}-$	-	0	$-C_3H_6-$	$-C_2H_4-$	1
CH_3-	$-C_5H_{10}-$	O	1	$-C_2H_4-$	$-C_3H_6-$	1
H-	$-C_{10}H_{20}-$	O	1	$-C_4H_8-$	$-C_4H_8-$	2
H-	$-C_{18}H_{36}-$	O	1	$-C_3H_6-$	$-C_2H_4-$	1
CH_3-	$-C_{20}H_{40}-$	O	1	$-C_2H_4-$	$-C_3H_6-$	2
H-	$-C_{16}H_{32}-$	O	1	$-C_3H_6-$	$-C_2H_4-$	1
CH_3-	$-C_6H_{12}-$	S	1	$-C_3H_6-$	$-C_2H_4-$	2
H-	$-C_{10}H_{20}-$	S	1	$-C_2H_4-$	$-C_3H_6-$	1
H-	$-C_{16}H_{32}-$	S	1	$-C_4H_8-$	$-C_2H_4-$	1
CH_3-	$-C_{14}H_{28}-$	S	1	$-C_5H_{10}-$	$-C_2H_4-$	4
H-	$-C_{18}H_{36}-$	S	1	$-C_3H_6-$	$-C_2H_4-$	1

Table 2

FORMULA:

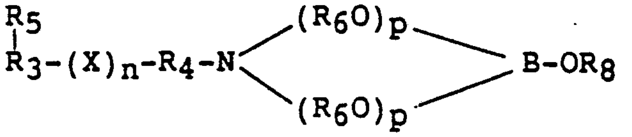


$$R_3-\underset{R_4OH}{\overset{R_5}{N}}-R_7-N\begin{matrix}(R_6O)pH\\(R_6O)pH\end{matrix}$$

III

R_5	R_3	R_4	R_7	R_6	P
H-	$-C_3H_6-$	$-CH_2-$	$-C_2H_4-$	$-C_2H_4-$	1
H-	$-C_6H_{12}-$	$-C_2H_4-$	$-C_3H_6-$	$-C_3H_6-$	2
H-	$-C_{12}H_{24}-$	$-C_3H_6-$	$-C_4H_8-$	$-C_2H_4-$	3
H-	$-C_{16}H_{32}-$	$-C_6H_{12}-$	$-C_5H_{10}-$	$-C_3H_6-$	1
H-	$-C_{18}H_{36}-$	$-C_3H_6-$	$-C_2H_4-$	$-C_2H_4-$	1
CH_3-	$-C_{17}H_{34}-$	$-C_4H_8-$	$-C_3H_6-$	$-C_2H_4-$	1
CH_3-	$-C_{20}H_{40}-$	$-C_2H_4-$	$-CH_2-$	$-C_2H_4-$	1
H-	$-C_{27}H_{54}-$	$-CH_2-$	$-CH_2-$	$-C_2H_4-$	1
CH_3-	$-C_{10}H_{20}-$	$-C_3H_6-$	$-C_2H_4-$	$-C_2H_4-$	2

The hydroxyl amine compounds may be used as such. However they may also be used in the form of an adduct or reaction product with a boron compound, such as a boric oxide a boron halide, a metaborate, boric acid, or a mono-, di-, and trialkyl borate. Such adducts or derivatives may be illustrated, for example, by the following structural formula:



IV

wherein R_3, R_4, R_5, R_6, X, n and p are the same as defined above, and wherein R_8 is either H or an alkyl radical.

Representative examples of alkyl borates which may be used to borate the alkanol amine compounds include mono-, di-, and tributyl borates, mono-, di-, and trihexyl borates, and the like. The borated adducts may be prepared simply by heating a mixture of the hydroxyl amine compound and the boron compound, preferably in the presence of a suitable solvent or solvents, preferably a hydrocarbon solvent. The presence of a solvent is not essential; however, if one is used it must be non-reactive. Reaction temperatures suitably may be on the order of about 100°C to about 280°C, preferably from about 125 to 175°C. Reaction time is not critical and, depending on the temperature, etc., it may vary from about 1-2 hours up to about 15 hours, e.g. 2 to 6 hours until the desired amount of water is removed. Such boration procedures are well known in the art and are described, for example, in U.S. Patents 4,529,528, 4,594,171, and 4,382,006, the disclosures of which are incorporated herein by reference.

The phosphosulfurized dispersant/detergent material contemplated for use in this invention may be prepared, for example, by treating the condensation product of a hydrocarbyl-substituted dicarboxylic acid or anhydride or ester derivative thereof and a polyamine, with an acidic reaction product of a phosphorous sulfide with a hydrocarbon

The long chain hydrocarbyl-substituted dicarboxylic acid material which can be used to make the dispersant includes the reaction product of long chain hydrocarbon polymer, generally a polyolefin,with (i) monounsaturated C_4 to C_{10} dicarboxylic acid wherein (a) the carboxyl groups are vicinal, (i.e. located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said monounsaturation; or with (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or diesters of (i). Upon reaction with the hydrocarbon polymer, the monounsaturation of the dicarboxylic acid material becomes saturated. Thus, for example, maleic anhydride becomes a hydrocarbyl-substituted succinic anhydride.

Typically, from about 0.7 to about 4.0 (e.g., 0.8 to 2.6), preferably from about 1.0 to about 2.0, and most preferably from about 1.1 to about 1.7 moles of said unsaturated C_4 to C_{10} dicarboxylic acid material are charged to the reactor per mole of polyolefin charged.

Normally, not all of the polyolefin reacts with the unsaturated acid or derivative and the hydrocarbyl-substituted dicarboxylic acid material will contain unreacted polyolefin. The unreacted polyolefin is typically not removed from the reaction mixture (because such removal is difficult and would be commercially infeasible) and the product mixture, stripped of any unreacted monounsaturated C_4 to C_{10} dicarboxylic acid material, is employed for further reaction with the amine or alcohol as described hereinafter to make the dispersant.

Characterization of the average number of moles of dicarboxylic acid, anydride or ester which have reacted per mole of polyolefin charged to the reaction (whether it has undergone reaction or not) is defined herein as functionality. Said functionality is based upon (i) determination of the saponification number of the resulting product mixture using potassium hydroxide; and (ii) the number average molecular weight of the polymer charged using techniques well known in the art. Functionality is defined solely with reference to the resulting product mixture. Consequently, although the amount of said reacted polyolefin contained in the resulting product mixture can be subsequently modified, i.e., increased or decreased by techniques known in the art, such mocdifications do not alter functionality as defined above. The term hydrocarbyl-substituted dicarboxylic acid material is intended to refer to the product mixture whether it has undergone such modification or not.

Accordingly, the functionality of the hydrocarbyl-substituted dicarboxylic acid material will be typically at least about 0.5, preferably at least about 0.8, and most preferably at least about 0.9, and can vary typically from about 0.5 to about 2.8 (e.g., 0.6 to 2), preferably from about 0.8 to about 1.4, and most preferably from about 0.9 to about 1.3.

Exemplary of such unsaturated mono and dicarboxylic acids, or anhydrides and esters thereof are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, etc.

Preferred olefin polymers for reaction with the unsaturated dicarboxylic acids or derivatives thereof are polymers comprising a major molar mount of C_2 to C_{10}, e.g. C_2 to C_5 monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of: ethylene and propylene; butylene and isobutylene; propylene and isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C_4 to C_{18} non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene: or a copolymer of ethylene, propylene and 1,4-hexadiene; etc.

In some cases, the olefin polymer may be completely saturated, for example an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

The olefin polymers used in the dispersants will usually have number average molecular weights within the range of about 700 and about 5,000, more usually between about 800 and about 3000. Particularly useful olefin polymers have number average molecular weights within the range of about 900 and about 2500 with approximately one terminal double bond per polymer chain. An especially useful starting material for highly potent dispersant additives is polyisobutylene. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information, see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

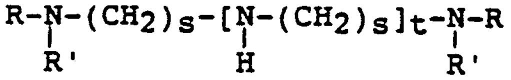
Processes for reacting the olefin polymer with the C_{4-10} unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the olefin polymer and the dicarboxylic acid or derivative may be simply heated together as disclosed in U.S. Patents 3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place. Or, the olefin polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polyolefin at a temperature of 60 to 250°C., e.g. 120 to 160°C., for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient unsaturated acid or derivative at 100 to 250°C., usually about 180 to 235°C., for about 0.5 to 10, e.g. 3 to 8 hours, so the product obtained will contain the desired number of moles of the unsaturated acid or derivative per mole of the halogenated polymer. Processes of this general type are taught in U.S. Patents 3,087,936, 3,172,892, 3,272,746 and others.

Alternatively, the olefin polymer, and the unsaturated acid or derivative are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in U.S. Patents 3,215,707, 3,231,587, 3,912,764, 4,110,349, and in U.K. 1,440,219.

By the use of halogen, about 65 to 95 wt. % of the polyolefin, e.g. polyisobutylene will normally react with the dicarboxylic acid or derivative. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 75 wt. % of the polyisobutylene will react. Chlorination helps increase the reactivity.

In order to form the phosphosulfurized additives that are used in this invention, the hydrocarbyl dicarboxylic material first must be neutralized with a polyfunctional amine. This will result in the formation of an imide or amide linkage, or a mixture of imide and amide linkages, in the hydrocarbyl dicarboxylic material and will add at least one reactive amino group thereto. As discussed more fully hereinbelow, the amino group will react with the phosphorous sulfide-hydrocarbon reaction product to provide the dispersants which are useful in this invention.

Useful amine compounds for neutralization of the hydrocarbyl substituted dicarboxylic material include polyamines of about 2 to 60, e.g. 3 to 20, most preferably 3 to 10, total carbon atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other non-interfering groups, e.g., alkoxy groups, amide groups, nitrile groups, imidazoline groups, and the like. Preferred amines are aliphatic saturated amines, including those of the general formula:



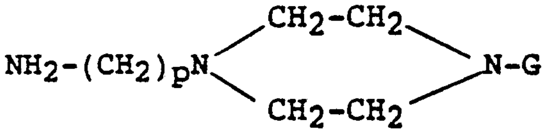
$$R\text{-}\underset{R'}{N}\text{-}(CH_2)_s\text{-}[\underset{H}{N}\text{-}(CH_2)_s]_t\text{-}\underset{R'}{N}\text{-}R$$

V

wherein R and R′ are independently selected from the group consisting of hydrogen; C_1 to C_{25} straight or branched chain alkyl radicals; C_1 to C_{12} alkoxy C_2 to C_6 alkylene radicals; and C_1 to C_{12} alkylamino C_2 to C_6 alkylene radicals; each s is the same or a different number of from 2 to 6, preferably 2 to 4; and t is a number of from 0 to 10, preferably 2 to 7. If $t=0$, then at least one of R or R^1 must be H such that there are at least two of either primary or secondary amino groups.

Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene) triamine; di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N-dodecyl-1,3-propane dimine; di-,and tri-tallow amines; amino morpholines such as N-(3-aminopropyl) morpholine; etc.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic compounds such as morpholines, imidazolines, and N-aminolakyl piperazines of the general formula:



VI

wherein G is independently selected from the group consisting of hydrogen and omega-(non-tertiary)-aminoalkylene radicals of from 1 to 3 carbon atoms, and p is a number of from 1 to 4. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine; etc.

Commercial mixtures of amine compounds advantageously may be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and isomeric piperazines. A low cost mixture of poly(ethyleneamine) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

Useful amines also include polyoxalkylene polyamines such as those of the formulas:

$NH_2\text{—alkylene—(O-alkylene)}_m\text{—}NH_2$ VII

where m has a value of about 3 to 70 and preferably 10 to 35; and

$R\ [\ \text{alkylene}\,(\text{O-alkylene})_n\text{-}NH_2]_a$ VIII

where n has a value of about 1 to 40 with the proviso that the sum of all the n's is from about 3 to about 70 and preferably from about 6 to about 35, R is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms, and a is a number from 3 to 6. The alkylene groups in either formula VII or VIII may be straight or branched chain containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

The above polyoxyalkylene polyamines, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from about 200 to about 4,000 and preferably from about 400 to about 2,000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weight ranging from about 200 to 2,000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc.

The amine is readily reacted with the selected hydrocarbyl-substituted dicarboxylic acid material, e.g. alkenyl succinic anhydride, by heating an oil solution containing 5 to 95 wt. % of said hydrocarbyl-substituted dicarboxylic acid material to about 100 to 250°C., preferably 125 to 175°C., generally for 1 to 10, e.g. 2 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides or mixtures of imides and amides, rather than amides and salts. Reaction ratios of hydrocarbyl-substituted dicarboxylic acid material to equivalents of amine as well as the other nucleophilic reactants described herein can vary considerably, depending on the reactants and type of bonds formed. Generally from 0.1 to 1.0, preferably from about 0.2 to 0.6, e.g., 0.4 to 0.6, equivalents of dicarboxylic acid unit content (e.g., substituted succinic anhydride content) is used per reactive equivalent of nucleophilic reactant, e.g., amine. For example, about 0.8 mole of a pentamine (having two primary amino groups and five reactive equivalents of nitrogen per molecule) is preferably used to convert into a mixture of amides and imides, a composition, having a functionality of 1.6, derived from reaction of polyolefin and maleic anhydride; i.e., preferably the pentamine is used in an amount sufficient to provide about 0.4 equivalents (that is, 1.6 divided by (0.8 x 5) equivalents) of succinic anhydride units per reactive nitrogen equivalent of the amine.

As indicated above, the hydrocarbyl-substituted dicarboxylic acid material-polyamine reaction products are further reacted with an acidic organic compound containing phosphorus and sulfur, more specifically with a phosphosulfurized hydrocarbon. In particular, the reaction products of the above type that are employed in the present invention are those that contain sufficient residual amino nitrogen to react with the acidic groups of the phosphosulfurized hydrocarbon, as will be more apparent in the ensuing description. To facilitate the ensuing discussion, the phosphorous and sulfur containing reactants may be referred to alternatively as organic thio-acids of phosphorus.

For convenience, the reaction product of the hydrocarbyl-substituted dicarboxylic acid material with the polyamine will be referred to as the amine-containing intermediate. As previously stated, the amine-containing intermediate must have sufficient amino nitrogen remaining so that reaction with the acidic groups of the organic thio-acid of phosphorous is possible.

The amine-containing intermediate may be reacted with the phosphosulfurized hydrocarbon in amounts sufficient to give partial or complete neutralization of the amine portion of the amine-containing intermediate. Since the potency of the amine- containing intermediate is related, in part, to its basicity, the ratio of amine to organic thio-acid of phosphorus is limited in practice by the balance of the several functions of this additive. That is, if all the amine functions are neutralized by stoichiometric amounts of organic thio-acids, the antioxidant and anti-wear properties of the additive are maximized at the expense of detergency or deposit control. Most advantageously, ratios of amine to thio-acid are chosen so that dispersancy, anti-wear and antioxidant potency are optimized. Generally if at least one amino group per mole of amine-containing intermediate is left unreacted, this optimization can be accomplished.

As little as 0.01 mole of the organic thio-acid of phosphorus may be reacted with 1 mole of the amine-containing intermediate. The maximum number of moles of the organic acid that can thus be reacted will depend on the number of amino nitrogen groups that are still available for neutralization in the intermediate, but normally complete neutralization of all of the amino groups is not desired. Generally, for each mole of amine-containing intermediate, in the range of about 0.1 to 0.2 mole of phosphosulfurized hydrocarbon will be sufficient to impart anti-wear and antioxidant properties, although higher ratios of the reactant may be used, as already discussed. For the purpose of ascertaining the molar equivalent of the phosphosulfurized hydrocarbon, it is assumed that all of the phosphorus in that material is available as a mono-basic acid. Reaction may be effected merely by mixing the reactants together and heating the mixture for from 1 to 6 hours, or more usually from 2 to 5 hours at a temperature in the range of from about 100°F, to about 400°F., e.g. 100 to 250°F., or more generally from about 150°F. to about 225°F. The reaction may by aided by blowing a stream of inert gas through the mixture during the heating period.

The phosphosulfurized hydrocarbons may be prepared by reaction of sulfide of phosphorus such as P_2S_3, P_2S_5, P_4S_7, P_4S_{10}, preferably P_2S_5, with a suitable hydrocarbon material such as a heavy petroleum fraction, a polyolefin, or a terpene or mixtures thereof.

The heavy petroleum fractions that may be employed include distillates or residua containing less than 5% of aromatics and having viscosities at 210°F. in the range of about 140 to 250 SUS.

The terpenes which may be used in this invention are unsaturated hydrocarbons having the formula $C_{10}H_{16}$, occuring in most essential oils and oleoresins of plants. The terpenes are based on the isoprene unit C_5H_8, and may be either acyclic or cyclic with one or more benzenoid groups. They are classified as monocyclic (dipentene), bicyclic (pinene), or acyclic (myrcene), according to the molecular structure. The preferred terpenes are bicyclic such as alpha-pinene and beta-pinene.

Suitable polyolefins include those having Staudinger molecular weights in the range of typically from about 500 to about 200,000, preferably from about 600 to about 20,000, and most preferably from about 800 to about 2,000, and containing from 2 to 6 carbon atoms per olefin monomer, e.g., ethylene, propylene, butylene, isobutylene, isoamylene and mixtures. Particularly preferred polyolefins are the polyisobutylenes having Staudinger molecular weights in the range of from about 700 to about 100,000.

The phosphosulfurized hydrocarbon can be prepared by reacting the hydrocarbon with from about 5 to 30 wt. percent of a sulfide of phosphorus, preferably with from about 10 to 20 wt. percent of phosphorous pentasulfide under anhydrous conditions at temperatures of from about 150 to about 600°F. for from about one-half to about 15 hours. The preparation of the phosphosulfurized hydrocarbons are well known in the art and are described, for example, in U.S. Patents 2,875,188, 3,511,780, 2,316,078, 2,805,217 and 3,850,822, the disclosures of which are incorporated herein by reference.

In a preferred aspect of this invention, the phosphosulfurized dispersant/detergent material is combined with the organic phosphite ester and hydroxyl amine compound, but in further combination with a borated ashless, sulfur and phosphorous-free dispersant. The description of the borated ashless dispersant corresponds to the description provided herein above in connection with the amine containing intermediate used in the formation of the phosphorous-and sulfur-containing dispersant, but which is further reacted with a boron compound.

The optional sulfur-and phosphorous-free ashless dispersant used as an additive per se, when borated, is referred to herein for convenience as borated, aminated dispersant.

Boration of the aminated dispersant can be carried out as generally taught in U.S. Patents 3,087,936 and 3,254,025, which patents are incorporated herein by reference. Such boration is readily accomplished by treating the aminated dispersant with a boron compound such as boric oxide, boron halides, and metaborate, boric acid, or a mono-, di-, and trialkyl borate in an mount to provide from about 0.1 atomic proportion of boron for each mole of the aminated dispersant composition to about 10 atomic proportions of boron for each atomic proportion of nitrogen of the dispersant composition. Generally, the borated, aminated dispersants contain from about 0.05 to 2.0 wt. %, e.g., 0.03 to 0.7 wt. % boron based on the total weight of said borated, aminated dispersant compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g. the metaborate salt of the diimide.

Treating is readily carried out by adding from about 0.05 to 4, e.g. 1 to 3 wt. % (based on the weight of said aminated dispersant compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said aminated dispersant and heating with stirring at from about 135°C to 190, e.g., 140-170°C., for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges. Or, the boron treatment can be carried out by adding boric acid to the hot reaction mixture of the dicarboxylic acid material and amine while removing water.

The combination of the organic phosphite esters, the hydroxyl amine compounds, and the phosphosulfurized hydrocarbons, and preferably, the borated, aminated hydrocarbyl-substituted dicarboxylic acid materials (referred to herein as borated, aminated dispersant) of the present invention has been found to possess multi-functional properties including anti-wear, friction modification, friction stability, and copper corrosion resistance properties.

Accordingly, the additive combination of the invention is used by incorporation and dissolution or dispersion into an oleaginous material such as fuels and lubricating oils.

The present combination of additives finds its primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed.

Such base oils may be natural or synthetic. Thus, base oils suitable for use in preparing lubricating compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Particularly advantageous results are achieved by employing the additive combination of the present invention in base oils conventionally employed in power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention.

Thus, the additive combination of the present invention may be suitably incorporated into synthetic base oils such as alkyl esters of dicarboxylic acids, polyglycols and alcohols; polyalphaolefins, alkyl benzenes, organic esters of phosphoric acids, polysilicone oil, etc.

Natural base oils include mineral lubricating oils which may vary widely as to their crude source, e.g. whether paraffinic, naphthenic, mixed paraffinic-naphthenic, and the like; as well as to their formation, e.g. distillation range, straight run or cracked, hydrofined, solvent extracted and the like.

More specifically, the natural lubricating oil based stocks which can be used in the compositions of this invention may be straight mineral lubricating oil or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been removed. The oils may be refined by conventional methods using acid, alkali, and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc.

The lubricating oil base stock conveniently has a viscosity of typically about 2.5 to about 12, and preferably about 3.5 to about 5 cst. at 100°C.

Thus the additive combination of the present invention can be employed in a lubricating oil composition which comprises lubricating oil, typically in a major amount, and the additive combination, typically in a minor amount, which is effective to impart enhanced friction modification, anti-wear, friction stability, and sludge inhibition properties relative to the absence of the additives. Additional conventional additives selected to meet the particular requirements of a selected type of lubricating oil composition can be included as desired.

The additive materials of this invention are oil soluble, dissolvable in oil with the aid of a suitable solvent, or are stably dispersible in oil. Oil soluble, dissolvable, or stably dispersible, as that terminology is used herein, does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the respective additives are soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the incorporation of an additional dispersant and/or other additives may also permit incorporation of higher levels of a particular organic phosphite ester, hydroxyl amine compound or phosphosulfurized hydrocarbon, if desired.

The additives of the present invention can be incorporated into the lubricating oil in any convenient way. Thus, they can be added directly to the oil by dispersing, or dissolving the same in the oil at the desired level of concentration typically with the aid of the suitable solvent such as benzene, xylene, toluene, tetrahydrofuran, ethers such as n-propyl ether, n-amyl ether or the like. Such blending can occur at room temperature or elevated temperatures. Alternatively, the organic phosphite ester and alkanol amine additive combination may be blended with a suitable oil-soluble solvent and base oil to form a concentrate, followed by blending the concentrate with lubricating oil base stock to obtain the final formulation.

The lubricating oil base stock for the additives of the present invention typically is adapted to perform a selected function by the incorporation of additives therein to form lubricating oil compositions (i.e., formulations).

As indicated above, one broad class of lubricating oil compositions suitable for use in conjunction with the additives of the present invention are power steering fluids, tractor fluids, tractor universal oils, and the like.

The benefits of the additives of the present invention are particularly significant when employed in a lubricating oil adapted for use as an automatic transmission fluid.

Power transmitting fluids, such as automatic transmission fluids, as well as lubricating oils in general, are typically compounded from a number of additives each useful for improving chemical and/or physical properties of the same. The additives are usually sold as a concentrate package in which mineral oil or some other base oil is present. The mineral lubricating oil in automatic transmission fluids typically is refined hydrocarbon oil or a mixture of refined hydrocarbon oils selected according to the viscosity requirements of the particular fluid, but typically would havea viscosity range of 2.5-9, e.g. 3.5-9 cst. at 100°C. Suitable base oils include a wide variety of light hydrocarbon mineral oils, such as naphthenic base oils, paraffin base oils, and mixtures thereof.

Representative additives which can be present in such packages as well as in the final formulation include viscosity index (V.I.) improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, lube oil flow improvers, dispersants, anti-foamants, anti-wear agents, detergents, metal rust inhibitors and seal swellants.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures.

V.I. improvers are generally high molecular weight hydrocarbon polymers or more preferably polyesters. The V.I. improvers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties.

These oil soluble V.I. polymers will generally have number average molecular weights of from 10^3 to 10^6, preferably 10^4 to 10^6, e.g. 20,000 to 250,000, as determined by gel permeation chromatography or membrane osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more monomers of C_2 to C_{30}, e.g. C_2 to C_8 olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic alkyl-aromatic, cycloaliphatic, etc. Frequently they will be of ethylene with C_3 to C_{30} olefins, particularly preferred being the copolymers of ethylene and propylene. Other polymers can be used such as polyisobutylenes, homopolymers and copolymers of C_6 and higher alpha olefins, atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene.

More specifically, other hydrocarbon polymers suitable as viscosity index improvers in the present invention include those which may be described as hydrogenated or partially hydrogenated homopolymers, and random, tapered, star, or block interpolymers (including terpolymers, tetrapolymers, etc.) of conjugated dienes and/or monovinyl aromatic compounds with, optionally, alpha-olefins or lower alkenes, e.g., C_3 to C_{18} alpha-olefins or lower alkenes. The conjugated dienes include isoprene, butadiene, 2,3-dimethylbutadiene, piperylene and/or mixtures thereof, such as isoprene and butadiene. The monovinyl aromatic compounds include vinyl di- or polyaromatic compounds, e.g., vinyl naphthalene, or mixtures of vinyl mono-, di-, and/or polyaromatic compounds, but are preferably monovinyl monoaromatic compounds, such as styrene or alkylated styrenes substituted at the alpha-carbon atoms of the styrene, such as alpha-methylstyrene, or at ring carbons, such as o-, m-, p-methylstyrene, ethylstyrene, propylstyrene, isopropyl-styrene, butylstyrene isobutylstyrene, tert-butylstyrene (e.g., p-tertbutylstyrene). Also included are vinylxylenes, methylethyl styrenes and ethylvinylstyrenes. Alpha-olfins and lower alkenes optionally included in these random, tapered and block copolymers preferably include ethylene, propylene, butene, ethylene-propylene copolymers, isobutylene, and polymers and copolymers thereof. As is also known in the art, these random, tapered and block copolymers may include relatively small amounts, that is less than about 5 moles, of other copolymerizable monomers such as vinyl pyridines, vinyl lactams, methacrylates, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl stearate, and the like.

Specific examples include random polymers of butadiene and/or isoprene and polymers of isoprene and/or butadiene and styrene. Typical block copolymers include polystyrene-polyisoprene, polystyrene-polybutadiene, polystyrene-polyethylene, polystyrene-ethylene propylene copolymer, polyvinyl cyclohexane-hydrogenated polyisoprene, and polyvinyl cyclohexane-hydrogenated polybutadiene. Tapered polymers include those of the foregoing monomers prepared by methods known in the art. Star-shaped polymers typically comprise a nucleus and polymeric arms linked to said nucleus, the arms being comprised of homopolymer or interpolymer of said conjugated diene and/or monovinyl aromatic monomers. Typically, at least about 80% of the aliphatic unsaturation and about 20% of the aromatic unsaturation of the star-shaped polymer is reduced by hydrogenation.

Representative examples of patents which disclose such hydrogenated polymers or interpolymers include U.S. Patent Nos. 3,312,621, 3,318,813, 3,630,905, 3,668,125, 3,763,044, 3,795,615, 3,835,053, 3,838,049, 3,965,019, 4,358,565, and 4,557,849, the disclosures of which are herein incorporated by reference.

The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and it may be oxidized and contain oxygen. Also included are derivatized polymers such as post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol, or amine, e.g. an alkylene polyamine or hydroxy amine, e.g. see U.S. Patents 4,089,794, 4,160,739, 4,137,185, or copolymers of ethylene and propylene reacted or grafted with nitrogen compounds such as shown in U.S. Patents 4,068,056, 4,068,058, 4,146,489 and 4,149,984.

Suitable hydrocarbon polymers are ethylene copolymers containing from 15 to 90 wt % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C_3 to C_{28}, preferably C_3 to C_{18}, more preferably C_3 to C_8, alpha-olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25 wt. % as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methyl-heptene-1, etc., and mixtures thereof.

Terpolymers, tetrapolymers, etc., of ethylene, said C_{3-28} alpha-olefin, and non-conjugated diolefin or mixtures of such diolefins may also be used. The amount of the non-conjugated diolefin generally ranges from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

The preferred V.I. improvers are polyesters, most preferably polyesters of ethylenically unsaturated C_3 to C_8 mono- and dicarboxylic acids such as methacrylic and acrylic acids, maleic acid, maleic anhydride, fumaric acid, etc.

Examples of unsaturated esters that may be used include those of aliphatic saturated mono alcohols of at least 1 carbon atom and preferably of from 12 to 20 carbon atoms, such as decyl acrylate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

Other esters include the vinyl alcohol esters of C_2 to C_{22} fatty or monocarboxylic acids, preferably saturated such as vinyl acetate, vinyl laureate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof. Copolymers of vinyl alcohol esters with unsaturated acid esters such as the copolymer of vinyl acetate with dialkyl fumarates, can also be used.

The esters may be copolymerized with still other unsaturated monomers such as olefins, e.g. 0.2 to 5 moles of C_2-C_{20} aliphatic or aromatic olefin per mole of unsaturated ester, or per mole of unsaturated acid or anhydride followed by esterification. For example, copolymers of styrene with maleic anhydride esterified with alcohols and amines are known, e.g. see U.S. Patent 3,702,300.

Such ester polymers may be grafted with, or the ester copolymerized with, polymerizable unsaturated nitrogen-containing monomers to impart dispersancy to the V.I. improvers. Examples of suitable unsaturated nitrogen-containing monomers to impart dispersancy include those containing 4 to 20 carbon atoms such as amino substituted olefins as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying a polymerizable ethylenically unsaturated substituent, e.g. the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 2-vinyl-pyridine, 3-vinyl-pyridine, 4-vinyl-pyridine, 3-methyl-5-vinyl-pyridine, 4-methyl-2-vinyl-pyridine, 4-ethyl-2-vinyl-pyridine and 2-butyl-5-vinyl-pyridine and the like.

N-vinyl lactams are also suitable, e.g. N-vinyl pyrrolidones or N-vinyl piperidones.

The vinyl pyrrolidones are preferred and are exemplified by N-vinyl pyrrolidone, N-(1-methyl-vinyl) pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3-dimethylpyrrolidone, N-vinyl-5-ethyl pyrrolidone, etc.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the non-ferrous metallic parts in contact with the fluid. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. As discussed hereinabove, the phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorous for 1/2 to 15 hours, at a temperature in the range of 150° to 400°F. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent 2,969,324.

Other suitable corrosion inhibitors include copper corrosion inhibitors comprising hydrocarbylthio-disubstitued derivatives of 1, 3, 4-thiadiazole, e.g., C_2 to C_{30}; alkyl, aryl, cycloalkyl, aralkyl and alkaryl-mono-, di-, tri-, or tetra- or thio-disubstituted derivatives thereof.

Representative examples of such materials included 2,5-bis(octylthio) 1,3,4-thiadiazole; 2,5-bis(octyldithio)-1,3,4-thiadiazole; 2,5-bis(octyltrithio)-1,3,4-thiadiazole; 2,5-bis(octyltetrathio)-1,3,4-thiadiazole; 2,5-bis(nonylthio)-1,3,4-thiadiazole; 2,5-bis(dodecyldithio)-1,3,4-thiadiazole; 2-dodecyldithio-5-phenyldithio-1,3,4-thiadiazole; 2,5-bis(cyclohexyldithio)-1,3,4-thiadiazole; and mixtures thereof.

Preferred copper corrosion inhibitors are the derivative of 1,3,4-thiadiazoles such as those described in U.S. Patents 2,719,125, 2,719,126, and 3,087,932, especially preferred is the compound 2,5-bis(t-octyldithio)-1,3,4-thiadiazole, commercially available as Amoco 150, and 2,5-bis(t-nonyldithio)-1,3,4-thiadiazole, commerically available as Amoco 158.

The preparation of such materials is further described in U.S. patents 2,719,125, 2,719,126, 3,087,932, and 4,410,436, the disclosures of which are hereby incorporated by reference.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Such oxidation inhibitors include alkaline earth metal salts of alkylphenol thioethers having preferable C_5 to C_{12} alkyl side chains, e.g. calcium nonylphenol sulfide, barium t-octylphenol sulfide;

aryl amunes, e.g. dioctylphenylamine, phenyl-alpha-naphthylamine; phosphosulfurized or sulfurized hydrocarbons, etc.

Friction modifiers serve to impart the proper friction characteristics to an ATF as required by the automotive industry. In the present invention, the hydroxyl amine compounds function as the primary friction modifier. However, the organic phosphite esters impart friction modification as well as anti-wear properties.

Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation. The primary dispersants to be used in accordance with this invention are the phosphosulfurized dispersant/detergent material described above. Lubricating oil flow improvers (LOFI) include all those additives which modify the, size, number, and growth of wax crystals in lube oils in such a way as to impart improved low temperature handling, pumpability, and/or vehicle operability as measured by such tests as pour point and mini rotary viscometry (MRV). The majority of lubricating oil flow improvers are polymers or contain polymers. These polymers are generally of two types, either backbone or sidechain.

The backbone variety, such as the ethylene-vinyl acetates (EVA), have various lengths of methylene segments randomly distributed in the backbone of the polymer, which associate or cocrystallize with the wax crystals inhibiting further crystal growth due to branches and non-crystalizable segments in the polymer.

The sidechain type polymers, which are the predominant variety used as LOFI's, have methylene segments as the side chains, preferably as straight side chains. These polymers work similarly to the backbone type except the side chains have been found more effective in treating isoparaffins as well as n-paraffins found in lube oils. Representative of this type of polymer are C_8-C_{18} dialkylfumarate/vinyl acetate copolymers, polyacrylates, polymethacrylates, and esterified styrene-maleic anhydride copolymers.

Foam control can be provided by an anti-foamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane.

Anti-wear agents, as their name implies, reduce wear of moving metallic parts. Representative of conventional anti-wear agents are the zinc dialkyl dithiophosphates, and the zinc diaryl dithiophosphates. It is an advantage of the present invention that supplemental anti-wear agents do not have to be employed and, in fact, can be excluded from the compositions of this invention.

Detergents and metal rust inhibitors include the metal salts of sulfonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz, overbased) metal salts, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents. They are usually produced by heating a mixture comprising an oil-soluble sulfonate or alkaryl sulfonic acid, with an excess of alkaline earth metal compound above that required for complete neutralization of any sulfonic acid present, and thereafter forming a dispersed carbonate complex by reacting the excess metal with carbon dioxide to provide the desired overbasing. The sulfonic acids are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as for example those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 30 carbon atoms such as for example haloparaffins, olefins that may be obtained by dehydrogenation of paraffins, polyolefins as for example polymers from ethylene, propylene, etc. The alkaryl sulfonates usually contain from about 9 to about 70 more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moiety.

The alkaline earth metal compounds which may be used in neutralizing these alkaryl sulfonic acids to provide the sulfonates includes the oxides and hydroxides, alkoxides, carbonates, carboxylate, sulfide, hydrosulfide, nitrate, borates and ethers of magnesium, calcium, and barium. Examples are calcium oxide, calcium hydroxide, magnesium acetate and magnesium borate. As noted, the alkaline earth metal compound is used in excess of that required to complete neutralization of the alkaryl sulfonic acids. Generally, the amount ranges from about 100 to about 220%, although it is preferred to use at least 125%, of the stoichiometric amount of metal required for complete neutralization.

Various other preparations of basic alkaline earth metal alkaryl sulfonates are known, such as those described in U.S. Patents 3,150,088 and 3,150,089, wherein overbasing is accomplished by hydrolysis of an alkoxide-carbonate complex with the alkaryl sulfonate in a hydrocarbon solvent/diluent oil.

Seal swellants include mineral oils of the type that provoke swelling, including aliphatic alcohols of 8 to 13 carbon atoms such as tridecyl alcohol, with a preferred seal swellant being characterized as an oil-soluble, saturated, aliphatic or aromatic hydrocarbon ester of from 10 to 60 carbon atoms and 2 to 4 linkages, e.g. dihexyl phthalate, as are described in U.S. Patent 3,974,081.

Some of these numerous additives can provide a multiplicity of effects e.g. a dispersant oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions, when containing these additives, typically are blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated in Table 3 as follows:

Table 3

Compositions	Vol%	Wt%
V.I. Improver	1-15	1-16
Corrosion Inhibitor	0.01-1	0.01-1.5
Oxidation inhibitor	0.01-1	0.01-1.5
Dispersant	0.1-7	0.1-8
Lube Oil Flow Improver	0.01-1	0.01-1.5
Detergents and Rust Inhibitors	0.01-10	0.01-3
Anti-Foaming Agents	0.001-0.1	0.001-0.15
Anti-wear Agents	0.001-15	0.001
Seal Swellant	0.1-5	0.1-6
Friction Modifiers	0.01-1	0.01-1.5
Mineral Oil Base	Balance	Balance

In broad sense therefore, the organic phosphite ester, the hydroxyl amine compound, and the dispersant/detergent additives of the present invention, when employed in a lubricating oil composition, typically in a minor amount, are effective to impart enhanced anti-wear, friction modification, and detergency properties thereto, relative to the same composition in the absence of the additive combination. Additional conventional additives selected to meet the particular requirements of a selected type of lubricating oil composition also can be included as desired.

Accordingly, while any effective amount of the organic phosphite ester additive can be incorporated into a lubricating oil composition, it is contemplated that such effective amount be sufficient to provide a given composition with an amount of the organic phosphite ester additive of typically from about 0.01 to about 10 (e.g., 0.01 to 5), preferably from about 0.05 to about 5.0 (e.g, 0.1 to 1.0), most preferably from about 0.2 to about 0.6 wt.%, based on the weight of said composition. Similarly, while any effective amount of the hydroxyl amine additive can be incorporated into an oil composition; it is contemplated that such effective amount be sufficient to provide said composition with an amount of the hydroxyl amine additive of typically from about 0.01 to about 10, preferably from about 0.05 to about 5 (e.g., 0.1 to 1), and most preferably from about 0.1 to about 0.5 wt.%, based on the weight of said composition; and it is contemplated that an effective amount of the dispersant material typically will be in the range of from about 0.1 to about 15 (e.g., 0.1 to 10), preferably from 1 to about 10, and most preferably from 2 to about 6 wt.% based on the weight of the composition. Thus, generally speaking, the weight ratio of the organic phosphite ester to the hydroxyl amine compound to the dispersant material in the final lubricating oil compositions of this invention will be on the order of from about 0.01-10: 0.01-10: 0.1-15.

As discussed above, the dispersant may comprise soley a phosphosulfurized dispersant. However, in a preferred embodiment of the invention, the dispersant comprises a mixture of a phosphosulfurized dispersant and a borated aminated dispersant. In this preferred embodiment, a portion of the phosphosulfurized dispersant is replaced with borated, aminated dispersant. Thus, while it is contemplated that any effective weight ratio of phosphosulfurized dispersant to borated, aminated dispersant may be incorporated into a lubricating composition, it is contemplated that such effective amount be sufficient to provide a weight ratio of from about 1:0 to about 1:4, preferably from about 1:0.25 to about 1:2, and most preferably from about 1:0.3 to about 1:1 of phosphosulfurized dispersant to borated, aminated dispersant. Typically, the borated, aminated dispersant is present in a lubricating oil composition in a range of from 0 to about 8 (e.g., 0 to 6), preferably from about 0.1 to about 5, and most preferably from about 0.25 to about 4 wt. % based on the weight of the composition.

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the organic phosphite ester and hydroxyl amine compounds together with the other additives (said concentrate additive mixture being referred to herein as an additive package) whereby the several additives can be added simultaneously to the base oil to form the lubricating oil compositions. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive package will typically by formulated to contain the organic phosphite ester, the hydroxyl amine compound and the dispersant material combination of this invention and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive package is combined with a predetermined amount of base lubricant. Thus, the organic phosphite ester, hydroxyl amine compound, and dispersant material can be added to small amounts of base oil or, optionally, to other compatible solvents, along with other desirable additives to form concentrates containing active ingredients in collective amounts of typically from about 25 to about 100, and preferably from about 65 to about 95, and most preferably from about 75 to about 90 wt.% additives in the appropriate proportions, with the remainder being base oil As is the case with lubricating oil compositions which contain the present combination of additives, the concentrates contemplated herein may contain a weight ratio of organic phosphite ester to hydroxyl amine compound to dispersant typically of from about 0.01-10: 0.01-10: 0.1-15. Similarly, the concentrates contemplated herein preferably contain both a phosphosulfurized dispersant and a borated, aminated dispersant. Thus, the weight ratio of phosphosulfurized dispersant to borated, aminated dispersant typically is from about 1:0 to about 4:1, preferably from about 1:0.25 to 1:2, and most preferably from about 1:0.3 to about 1:1.

The final formulation may employ typically about 10 wt. % of the additive package with the remainder being base oil.

All of said weight percents expressed herein are based on active ingredient (a.i.) content of the additive, and/or upon the total weight of any additive package, or formulation which will be the sum of the a.i. weight of each additive plus the weight of total oil or diluent.

As noted above, the organic phosphite esters contemplated for use in this invention are characterized as possessing good friction modification properties as well as anti-wear properties. This has the added benefit of permitting a reduction in the amount of hydroxyl amine compound or other friction modifier needed to achieve the overall desired friction modification. It has been found that as the amount of hydroxyl amine compound or other friction modifier increases in an ATF, the lower the breakaway static torque becomes. As the breakaway static torque (as well as the breakaway static coefficient of friction) decreases, the bands of the automatic transmission become increasingly more susceptible to slippage. Consequently, it is extremely advantageous to be able to control, e.g. reduce, the amount of friction modifier (and hence also any associated friction stability promoter) without sacrificing the friction modifying properties of the fluid, e.g., as measured by the torque differential T_0-T_D and stability thereof, since this facilitates the simultaneous achievement of both the desired breakaway static torque and torque differential friction characteristics. It has also been found that the use of a phosphosulfurized dispersant, together with a borated, aminated dispersant, in further combination with the organic phosphite ester and the hydroxyl amine additives, results in a lubricating oil that possesses excellent friction durability and reduced corrosivity relative to an additive combination that does not include the borated, aminated dispersant.

In short, the combination of the organic phosphite ester, the hydroxyl amine compound and a phosphosulfurized hydrocarbon dispersant permit the formulator to flexibly tailor an ATF in order to achieve the balance of properties required under today's more stringent transmission manufacturers' specifications.

The following examples are given as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples. All parts and percentages in the examples as well as in the remainder of the specification and claims are by weight unless otherwise specified.

EXAMPLE 1

Part A

A polyisobutenyl succinic anhydride (PIBSA) having a succinic anhydride (SA) polyisobutylene (PIB) ratio (SA:PIB) i.e. functionality, of 1.04 was prepared by heating a mixture of 100 parts of polyisobutylene (PIB) having an M_n of 940 with 13 parts of maleic anhydride to a temperature of about 220°C. When the temperature reached 120°C, chlorine addition was begun and 1.05 parts of chlorine at a constant rate were added to the hot mixture for about 5 hours. The reaction mixture was then heat soaked at 220°C. for about 1.5 hours and then stripped with nitrogen for about 1 hour. The resulting polyisobutenyl succinic anhydride had an ASTM Saponification Number of 112 which calculates to a succinic anhydride (SA) to polyisobutylene (PIB) ratio (functionality) of 1.04 based upon the starting PIB as follows:

$$\text{SA:PIB ratio} = \frac{\text{SAP} \times M_n}{112200-(96 \times \text{SAP})} = \frac{112 \times 940}{112200-(96 \times 112)} = 1.04$$

The PIBSA product was 90 wt. % active ingredient (a.i.), the remainder being primarily unreacted PIB. The SA:PIB ratio of 1.04 is based upon the total PIB charged to the reactor as starting material, i e., both the PIB which reacts and the PIB which remains unreacted.

Part B

The PIBSA of Part A was aminated as follows: 1500 grams (1.5 moles) of the PIBSA and 1666 grams of S150N lubricating oil (solvent neutral oil having a viscosity of about 150 SSU at 100°C.) were mixed in a reaction flask and heated to about 149°C. Then, 193 grams (1 mole) of a commercial grade of polyethyleneamine which was a mixture of polyethyleneamines averaging about 5 to 7 nitrogen per molecule, hereinafter referred to as PAM, was added and the mixture was heated to 150°C. for about 2 hours; followed by 0.5 hours of nitrogen stripping, then cooling to give the final product (PIBSA-PAM). This product had a viscosity of 140 cs. at 100°C., a nitrogen content of 2.12 wt. % and contained approximately 50 wt. % PIBSA-PAM and 50 wt. % unreacted PIB and mineral oil (S150N).

Part C

A phosphosulfurized olefin was prepared by reacting 4.9 parts by weight of alpha-pinene with 1 part by weight of phosphorous pentasulfide for about 5 hours at temperatures in the range of 180 to 250°C. During the reaction the mixture was stirred and blown with nitrogen to eliminate the hydrogen sulfide that was evolved. The resulting phosphosulfurized olefin analyzed about 5 wt. percent of phosphorus and about 13 wt. percent of sulfur. Its viscosity at 210°F. was about 27 CST. For convenience in handling in subsequent reactions, the product was diluted with a S150N mineral oil to form a 65 wt. percent concentrate.

Part D

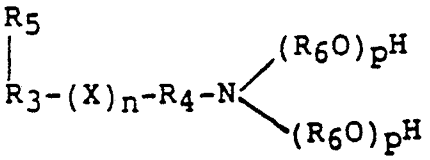
A phosphosulfurized PIBSA-PAM dispersant was prepared by reacting 18 parts by weight of the PIBSA-PAM reaction product formed in Part B with 6 parts by weight of the phosphosulfurized alpha-pinene formed in Part C at a temperature in the range of 100 to 130°C about 2 hours, after which the reaction was purged with nitrogen at about 120°C for an additional hour. The resulting product had an active ingredient concentration of about 52%, with the remainder being unreacted PIB and diluent oil.

EXAMPLE 2

A PIBSA-PAM was prepared in accordance with the precedure of EXAMPLE 1, Part B, except that a mole ratio of PIBSA:PAM of 2.2:1 was used. The resulting PIBSA-PAM was borated by mixing 98 parts by weight of the PIBSA-PAM with 2 parts by weight of boric acid. The mixture was heated to 160°C while stirring and blowing the reaction mass with nitrogen. The mixture was kept at 160°C for 2 hours, sparged with nitrogen for 1 hour and filtered. The resulting product was analyzed for 0.35 % boron.

EXAMPLE 3

A hydroxyl amine of the formula:



$$\overset{\displaystyle R_5}{\overset{|}{R_3}}-(X)_n-R_4-N\begin{cases}(R_6O)_pH\\(R_6O)_pH\end{cases}\qquad \text{II}$$

wherein n is 1; X is O; R_3 is a C_{18} aliphatic hydrocarbon radical; R_5 is H; R_4 is C_3 alkylene; R_6 is C_2 alkylene; and p is 1 was prepared by first reacting 270 parts by weight of octadecyl alcohol with 53 parts by weight of acrylonitrile in the presence of KOH at a temperature in the range of 100 to 110°F. for about 18 hours to form an ether nitrile intermediate. The intermediate was then hydrogenated in the presence of a Raney Nickel catalyst at a temperature in the range of from 270° to 280°F. until 2 moles of hydrogen had been absorbed. The ether amine was then reacted with 88 parts by weight of ethylene oxide at a temperature in the range of about 280°F. for 12 hours to form the hydroxyl amine product.

EXAMPLE 4

An ATF base fluid, designated hereinafter as the Test Base, was formulated with conventional amounts of seal swell additive, corrosion inhibitor, antioxidant, viscosity index improver and mineral oil base.

To a sample of the Test Base there was added 4 wt. % of the phosphosulfurized PIBSA-PAM dispersant of EXAMPLE 1, Part D, together with 0.3 wt. % of dioleyl phosphite and 0.3 wt. % of a hydroxyl amine friction modifier in accordance with formula II of EXAMPLE 3 above, wherein n is 0, R_3 is hydrogen, R_4 and R_5, combined, are a C_{18} aliphatic hydrocarbon radical, m is 2 and p is 1. The hydroxyl amine compound is a commercial product which is available under the trade designation Ethomeen 18-12 from the Armak Chemical Division of Akzo Chemie. The resulting formulation is designated Formulation 1.

To another sample of the Test Base there was added 4 wt. % of the borated PIBSA-PAM dispersant of Example 2, 0.3 wt. % of dioleyl phosphite and 0.3 wt. % of the same hydroxyl amine friction modifier that was used in Formulation 1. The resulting formulation is designated Comparative Formulation 2C.

To another sample of the Test Base there was added 4 wt.% of the phosphosulfurized PIBSA-PAM dispersant of EXAMPLE 1, Part D, 0.3 wt. % of dioleyl phosphite and 0.3 wt.% of the hydroxyl amine friciton modifier of EXAMPLE 3. The resulting formulation is designated Formulation 3.

To another sample of the Test Base there was added 4 wt.% of the borated PIBSA-PAM of EXAMPLE 2, 0.3 wt. % of dioleyl phosphite and 0.3 wt. % of the hydroxyl amine friction modifier of EXAMPLE 3. The resulting formulation is designated Comparative Formulation 4C.

To another sample of the Test Base there was added 4 wt. % of the phosphosulfurized PIBSA-PAM dispersant of EXAMPLE 1, Part D, along with 0.5 wt. % of dioleyl phosphite, and 0.2 wt. % of the hydroxyl amine friciton modifier that was used in Formulation 1. The resulting formulation is designated Formulation 5.

To another sample of the Test Base there was added 4 wt. % of the phosphosulfurized PIBSA-PAM dispersant of EXAMPLE 1, Part D, together with 0.5 wt. % of triphenyl phosphite and 0.2 wt. % of the hydroxyl mine friction modifier that was used in Formulation 1. The resulting formulation is designed Comparative Formulation 6C.

To another sample of the Test Base there was added 4 wt. % of the phosphosulfurized PIBSA-PAM dispersant that was used in Formulation 1, together with 0.3 % wt. of dioleyl phosphite and 0.3 wt. % of tetraethylene pentaamine. The resulting formulation is designed at Comparative Formulation 7C.

To another sample of the Test Base there was added 3 wt. of the phosphosulfurized PIBSA-PAM that was used in Formulation 1, together with 1.5 wt. of the borated PIBSA-PAM of EXAMPLE 2, 0.5 wt. of dioleyl phosphite, and 0.15 wt. of the hydroxyl amine friction modifier that was used in Formulation 1. The resulting formulation is designated Formulation 8.

To another sample of the Test Base there was added 3 wt. % of the phosphosulfurized PIBSA-PAM that was used in Formulation 1, together with 1.5 wt. % of the borated PIBSA-PAM of EXAMPLE 2 0.5 wt. % of dioleyl phosphite, and 0.15 wt. % of the hydroxyl amine friction modifier that was used in Formulation 3. The resulting formulation is designated Formulation 9.

The compositions of Formulations 1-9 are summarized in Table 4 as follows:

TABLE 4

Component, wt.%	Formulation Number				
	1	2C	3	4C	5
phosphosulfurized PIBSA-PAM	4.0	---	4.0	---	4.0
borated PIBSA-PAM	---	4.0	---	4.0	---
dioleyl phosphite	0.3	0.3	0.3	0.3	0.5
triphenyl phosphite	---	---	---	---	---
hydroxyl amine, n=0	0.3	0.3	---	---	0.2
hydroxyl amine, n=1, X=O	---	---	0.3	0.3	---
tetraethylene pentamine	---	---	---	---	---
Test Base	95.4	95.4	95.4	95.4	95.3

TABLE 4 CONTINUED

Component, wt.%	Formulation Number			
	6C	7C	8	9
phosphosulfurized PIBSA-PAM	4.0	4.0	3.0	3.0
borated PIBSA-PAM	---	---	1.5	1.5
dioleyl phosphite	---	0.3	0.5	0.5
triphenyl phosphite	0.5	---	---	---
hydroxyl amine, n=0	0.2	---	0.15	---
hydroxyl amine, n=1, X=O	---	---	---	0.15
tetraethylene pentamine	---	0.3	---	---
Test Base	95.3	95.4	94.85	94.85

The Formulations 1 to 9 were then tested in accordance with a modified SAE No. 2 Friction Test.

THE MODIFIED SAE NO. 2 FRICTION TEST

This test uses a SAE No. 2 type friction machine operated successfully for 1000 cycles wherein no unusual clutch plate wear or composition-face plate flaking occurs. The test is conducted in a continuous series of 20 second cycles, each cycle consisting of three phases as follows: Phase I (10 seconds) - motor on at speed of 3,600 rpm, clutch plates disengaged; Phase II (5 seconds) - motor off, clutch plates engaged; and Phase III (5 seconds) - motor off, clutch plates released. 1000 cycles are repeated using 11,600 ft./lbs. of flywheel torque at 40 psig of applied clutch pressure. During the clutch engagement, friction torque is recorded as a function of time as the motor speed declines from 3600 rpm to 0. From the torque traces, the dynamic torque (T_{1800}) is determined midway between the start and end of clutch engagement (i.e. at a motor speed of 1800 rpm), as well as the torque at 200 rpm (T_{200}). The amount of time in seconds in phase II it takes for the motor speed to go from 3600 to 0 rpm is referred to as the lock-up time. The torque ratio of the oil formulation is then determined from (T_{200}/T_{1800}) as is the torque difference (T_{200}-T_{1800}). In addition to determining midpoint dynamic torque (T_{1800}) and torque at 200 rpm (T_{200}), the breakaway static torque (T_S) is also determined. This is achieved by rotating the composition plates at 1 to 5 rpm under a load of 40 psi. while locking the steel reaction plates and preventing them from rotating. The torque is then measured until slippage occurs. The maximum torque observed is recorded as T_S. From T_S is determined the Breakaway Static Torque ratio (T_S/T_{1800}).

The breakaway static torque ratio expresses the ability of the transmission to resist slippage; the lower the ratio, the higher the slippage.

The test results for Formulations 1-9 are shown in Table 5. The data reported in Table 5 is derived from the 1000th cycle.

TABLE 5

Data After 1000 Cycles	1	2C	3	4C	5	6C	7C	8	9
Torque @ 1800 rpm (T_{1800}), nm	130	127	129	127	136	132	112	131	119
Torque @ 200 rpm (T_{200}), nm	119	99	128	104	134	140	150	129	116
Static Breakaway Torque (T_s), nm	76	53	93	64	95	110	141	107	85
T_{200}/T_{1800}	0.92	0.78	0.99	0.82	0.985	1.06	1.3	0.98	0.93
$T_{200}-T_{1800}$	-11.0	-28.0	-0.8	-23.0	-2.0	+8.0	+38.0	-2.0	-3.0

Referring to Table 5, it can be seen that the breakaway static torque T_S is substantially lower for Comparative Formulation 2C than it is for Formulation 1. This is also true for Comparative Formulation 4C relative to Formulation 3. Accordingly, it will be apparent that the use of Comparative Formulations 2C and 4C would be more likely to result in clutches slipping in an actual vehicle than would the use of Formulations 1 and 3, respectively. Similarly, Formulations 1 and 3 are characterized by superior ratios of T_{200}/T_{1800} than are the Comparative Formulations 2C and 4C. With respect to the torque ratio, T_{200}/T_{1800}, an acceptable range for this parameter is from about, 0.9 to about 1.0. Values lower than 0.9 can result in slipping clutches and values higher than 1.0 cause very harsh unacceptable shifts. Both of Formulations 1 and 3 fall within the acceptable range for T_{200}/T_{1800}, whereas both of Comparative Formulation 2C and 4C are outside the acceptable range and would result in slipping clutches in actual use. With respect to T200-T1800, also known as delta torque, values in the zero to about -10 nm range give acceptably smooth shift performance. As can be seen in Table 2, both of Comparative Formulations 2C and 4C have a delta torque outside of the acceptable range, whereas the delta torque of Formulation 1 is just about at the upper limit of the acceptable range and the delta torque of Formulation 3 well within the acceptable range.

The data in Table 5 thus demonstrate the superiority of the present 3-component additive combination over a similar 3-component additive combination wherein a commercial borated PIBSA-PAM dispersant is substituted for the phosphosulfurized PIBSA-PAM dispersant of the invention.

The data in Table 5 also demonstrate the advantage that can be realized by using Formulation 5, rather than Comparative Formulation 6C, which contains an organic phosphite anti-wear agent i.e., triphenyl phosphite which is outside the scope of the invention. The data show that while the delta torque is within the acceptable range for both Formulations 5 and 6C, the ratio of T_{200}/T_{1800} for Comparative Formulation 6C is slightly higher than desirable.

Comparative Formulation 7C, which uses an mine compound in place of the hydroxyl mine friction modifying compound of the invention, has both a delta torque and a torque ratio which are unacceptable.

The data in Table 5 at Runs 8 and 9 also show that by replacing a portion of the phosphosulfurized PIBSA-PAM with a borated PIBSA-PAM dispersant, acceptable formulations can be prepared using less friction modifier, i.e. 0.15 wt.%, as opposed to 0.2%, as used, for example, in Formulation 5.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

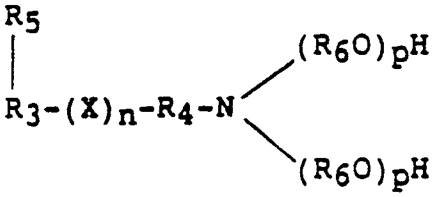
Claims

1. A lubricating oil composition adaptable for use as a power transmitting fluid which comprises:

(a) lubricating oil;

(b) a dispersing amount of a phosphosulfurized dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said adjacent carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) phosphosulfurized hydrocarbon, said hydrocarbon being selected from the group consisting of heavy petroleum fraction, polyolefin and terpene;

(c) a friction modifying amount of hydroxyl amine compound having at least one of the following formulas II or III:



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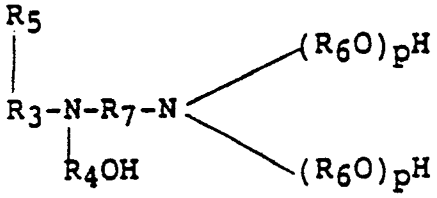
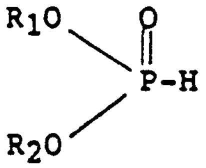


III

wherein R_3 represents a C_3-C_{27} saturated or unsaturated aliphatic hydrocarbon radical; R_4 represents a straight or branched chain C_1-C_6 alkylene radical; R_5 represents H or CH_3; R_6, independently, represents a straight or branched chain C_2-C_5 alkylene radical; R_7 represents a straight or branched chain C_1-C_5 alkylene radical; p, independently, is an integer of from 1 to 4, X represents O or S; and n represents 0 or 1; said hydroxyl amine compound having from about 10 to about 30 total carbon atoms; and

(d) an mount of an organic phosphite ester effective to impart both anti-wear and friction modification to the composition, said organic phosphite ester having the formula:



I

wherein R_1 and R_2, independently, represent the same or different C_{12}-C_{24} saturated or unsaturated, straight or branched chain hydrocarbyl radical having at most two unsaturated linkages.

2. The lubricating oil composition of claim 1, wherein R_3 represents a C_{16}-C_{20} alkylene radical and R_4 represents a C_2-C_4 alkylene radical.

3. The lubricating oil composition of claim 1 or claim 2, wherein R_3 is a C_{18} saturated or unsaturated aliphatic hydrocarbon radical, R_4 is C_3 alkylene, R_5 is H, R_6 is C_2 alkylene and p is 1.

4. The lubricating oil composition of according to any of the preceding claims wherein, based on the weight of said composition, said phosphosulfurized dispersant material (b) is present in an amount of from about 0.1 to about 15 wt% said hydroxyl amine compound (c) is present in an amount of from about 0.1 to about 10 wt%, and said organic phosphite (d) is present in an amount of from about 0.01 to about 10 wt%.

5. The lubricating oil composition of any of the preceding claims further comprising a dispersing amount of a borated, aminated dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl substituted dicarboxylic acid material having a functionality of from about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said adjacent carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) borating agent selected from at least one member of the group consisting of boric oxide, boron halide, metaborate, boric acid, mono-, di-, and trialkyl borate.

6. The lubricating oil composition of claim 5, wherein, based on the weight of said composition, said phosphosulfurized dispersant material (b) is present in an amount of from about 0.1 to about 15 wt.%, said hydroxyl mine compound (c) is present in an amount of from about 0.1 to about 10 wt.%, and said organic phosphite (d) is present in an mount of from about 0.01 to about 10 wt.%.

7. The lubricating oil composition of any of the preceding claims wherein R_1 and R_2 represent the oleyl radical.

8. The lubricating oil composition of claim 7, wherein the weight ratio of said phosphosulfurized dispersant to said borated, aminated dispersant in said composition is from about 1:0 to about 1:4.

9. The lubricating oil composition of claim 1, wherein said friction modifying hydroxyl amine compound is characterized by formula II and R_4 is a straight chain alkylene radical.

10. The lubricating oil composition of any of the preceding claims wherein R_1 and R_2 represent the oleyl radical.

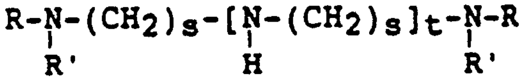
11. The lubricating oil composition of any of the preceding claims wherein, in said phosphosulfurized dispersant material (b), reactive component (i) (a) is polyisobutenyl-substituted succinic anhydride

material.

12. The lubricating oil composition of any of the preceding claims, wherein said phosphosulfurized hydrocarbon is derived from the reaction of alpha-pinene and P_2S_5.

13. The lubricating oil composition of any of the preceding claims, wherein said polyamine component (i) (b) is selected from the group consisting of polyamines having about 2 to 60 total carbon atoms and about 2 to 12 nitrogen atoms in the molecule.

14. The lubricating oil composition of claim 13, wherein said polymine is an aliphatic saturated mine having the general formula:



$$R-\underset{R'}{N}-(CH_2)_s-[\underset{H}{N}-(CH_2)_s]_t-\underset{R'}{N}-R \qquad V$$

wherein R and R′, independently, are the same or different and are selected from the group consisting of hydrogen, C_1 to C_{25} straight or branched chain alkyl radicals, C_1 to C_{12} alkoxy C_2 to C_6 alkylene radicals, and C_1 to C_{12} alkylmino C_2 to C_6 alkylene radicals; each s is the same or a different number of from 2 to 6; and t is a number of from 0 to 10, with the proviso that when $t=0$, at least one of R or R′ must be H such that there are at least two of either primary or secondary amino groups.

15. The lubricating oil composition of claim 13 or claim 14, wherein said polyamine is a mixture of poly(ethylene-amines) averaging about 5 to about 7 nitrogen atoms per molecule.

16. The lubricating oil composition of claim 13, wherein said polymine is a polyoxyalkylene polyamine having the formula:

$NH_2-\text{alkylene}-(\text{O-alkylene})_m-NH_2$ VII

where m has a value of about 3 to 70; or

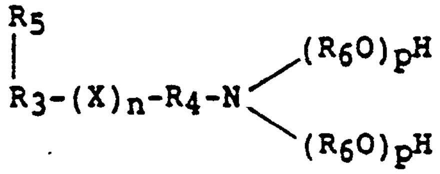
$R-[\text{alkylene}-(\text{O-alkylene})_n-NH_2]_a$ VIII

where n has a value of about 1 to 40 with the provision that the sum of all the n's is from about 3 to about 70, R is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms, and a is a number from 3 to 6.

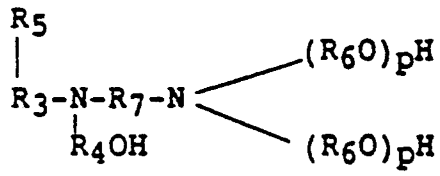
17. An additive concentrate comprising a base oil in oil in an amount up to about 75 wt. % and from about 25 wt. up to about 100 wt. % of said concentrate of a mixture comprised of:

a) phosphosulfurized dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of about 0.5 to about 2.8 and being derived from poly-olefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the car-boxyl groups are located on adjacent carbon atoms and at least one of said adjacent carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) phosphosulfurized hydrocarbon, said hydrocarbon being selected from the group consisting of heavy petroleum fraction, polyolefin and terpene;

b) friction modifying hydroxyl amine compound having at least one of the following formulas II or III:



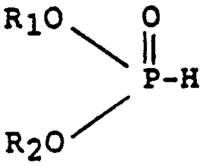
II



III

wherein R_3 represents a C_3-C_{27} saturated or unsaturated aliphatic hydrocarbon radical; R_4 represents a straight or branched chain C_1-C_6 alkylene radical; R_5 represents H or CH_3; R_6, independently, represents a straight or branched chain C_1-C_5 alkylene radical; a straight or branched chain C_2-C_5 alkylene radical; p, independently, is an integer of from 1 to 4, X represents O or S; and n represents 0 or 1; said hydroxyl amine compound having from about 10 to about 30 total carbon atoms; and

(c) an anti-wear and friction modifying organic phosphite ester having the formula:



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wherein R_1 and R_2, independently, represent the same or different C_{12}-C_{24} saturated or unsaturated, straight or branched chain hydrocarbyl radical having at most two unsaturated linkages;
said phosphosulfurized dispersant (a), said hydroxyl mine compound (b) and said organic phosphite ester (c) being present in said concentrate in a weight ratio of (a): (b): (c) of from about 0.01-10: 0.01-10: 0.1-15.

18. The concentrate of claim 17, wherein R_3 represents a C_{16}-C_{20} alkylene radical and R_4 represents a C_2-C_4 alkylene radical.

19. The concentrate of claim 17 or claim 18, wherein R_3 is a C_{18} saturated or unsaturated aliphatic hydrocarbon radical, R_4 is C_3 alkylene, R_5 is H, R_6 is C_2 alkylene and p is 1.

20. The concentrate of any of claims 17 to 19, wherein R_1 and R_2 represent the oleyl radical.

21. The concentrate of any one of claims 17 to 20, further comprising a dispersing amount of a borated, aminated dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of from about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said adjacent carbon atoms is part of said unsaturation, and (b) polyamine; and (ii) borating agent selected from at least one member of the group consisting of boric oxide, boron halide, metaborate, boric acid, mono-, di-, and trialkyl borate; wherein the weight ratio of the said phosphosulfurized dispersant, together with said borated, aminated dispersant, to said hydroxyl amine compound and said organic phosphite ester in said concentrate is from about 0.01-10: 0.01-10: 0.1-15.

22. The concentration of claim 21, wherein the weight ratio of said phosphosulfurized dispersant to said borated, aminated dispersant in said concentrate is from about 1:0 to about 1:4.

23. The concentrate of any of claims 17 to 22, wherein said hydroxyl amine compound is characterized by formula II and R_4 is a straight chain alkylene radical.

24. The concentrate of any of claims 17 to 23, wherein, in said phosphosulfurized dispersant material (b) reactive component (i) (a) is polyisobutenyl-substituted succinic anhydride material.

25. The concentrate of any of claims 17 to 24, wherein said phosphosulfurized hydrocarbon is derived from the reaction of alpha-pinene and P_2S_5.

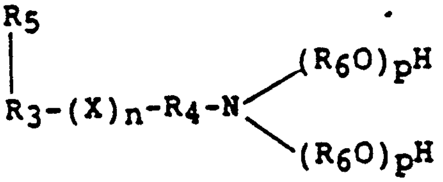
26. The concentrate of any of claims 17 to 25, wherein said polyamine reactive component (i) (b) is selected from the group consisting of polyamines having about 2 to 60 total carbon atoms and about 2 to 12 nitrogen atoms in the molecule.

27. The concentrate of claim 25 or claim 26, wherein said polyamine is a mixture of poly(ethyleneamines) averaging about 5 to about 7 nitrogen atoms per molecule.

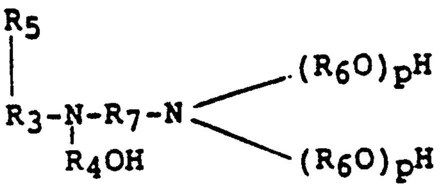
28. An additive concentrate comprising from about 5 to about 35 wt% base oil and from about 65 to about 95 wt% of said concentrate of a mixture comprised of:

(a) phosphosulfurized dispersant material comprising the reaction product of (i) the reaction product of polyisobutenyl succinic anhydride, wherein said polyisobutenyl group has a number average molecular weight of from about 700 to about 5,000, and polyamine, and (ii) the reaction product of sulfide of phosphorous and hydrocarbon selected from the group consisting of heavy petroleum fractions, terpene and polyolefin;

(b) a friction modifying hydroxyl amine compound having at least one of the following formulas II or III:



II



III

wherein R_3 represents a C_3-C_{27} saturated or unsaturated aliphatic hydrocarbon radical; R_4 represents a straight or branched chain C_1-C_6 alkylene radical; R_5 represents H or CH_3; R_6, independently, represents a straight or branched chain C_2-C_5 alkylene radical; R_7 represents a straight or branched chain C_1-C_5 alkylene radical; p, independently, is an integer of from 1 to 4, X represents O or S; and n represents 0 or 1; said hydroxyl mine compound having from about 10 to about 30 total carbon atoms; and

(c) dioleyl monohydrogen phosphite; said components (a), (b) and (c) being present in a weight ratio of 0.01-10: 0.01-10: 0.1-15.

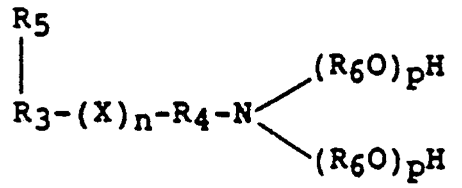
29. The additive concentrate of claim 28, further comprising a dispersing amount of borated, aminated dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of from about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) borating agent selected from at least one member of the group consisting of boric oxide, boron halide, metaborate, boric acid, mono-, di-, and trialkyl borate; wherein the weight ratio of the said phosphosulfurized dispersant, together with said borated, aminated dispersant, to said hydroxyl mine compound and said organic phosphite ester in said concentrate is from about 0.01-10: 0.01-10: 0.1-15.

30. An automatic transmission fluid which comprises a lubricating oil according to any one of claims 1 to 16.

31. The use for improving at least one of the properties of anti-wear, friction modification and dispersance of a lubricating oil adaptable for use as a power transmitting fluid, of an additive composition comprising:

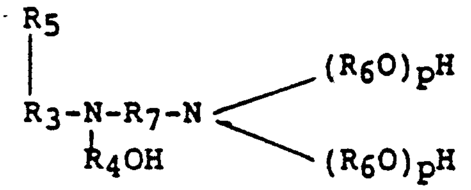
(a) a dispersing amount of a phosphosulfurized dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said adjacent carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) phosphosulfurized hydrocarbon, said hydrocarbon being selected from the group consisting of heavy petroleum fraction, polyolefin and terpene;

(b) a friction modifying amount of hydroxyl amine compound having at least one of the following formulas II or III:



$$\overset{\overset{\displaystyle R_5}{|}}{R_3}-(X)_n-R_4-N\genfrac{}{}{0pt}{}{\diagup(R_6O)_pH}{\diagdown(R_6O)_pH}$$

II

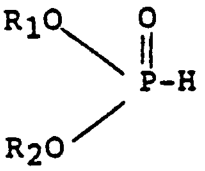


$$\overset{\overset{\displaystyle R_5}{|}}{R_3}-\underset{\underset{\displaystyle R_4OH}{|}}{N}-R_7-N\genfrac{}{}{0pt}{}{\diagup(R_6O)_pH}{\diagdown(R_6O)_pH}$$

III

wherein R_3 represents a C_3-C_{27} saturated or unsaturated aliphatic hydrocarbon radical; R_4 represents a straight or branched chain C_1-C_6 alkylene radical; R_5 represents H or CH_3; R_6, independently, represents a straight or branched chain C_2-C_5 alkylene radical; R_7 represents a straight or branched chain C_1-C_5 alkylene radical; p, independently, is an integer of from 1 to 4, X represents O or S; and n represents 0 or 1; said hydroxyl amine compound having from about 10 to about 30 total carbon atoms; and

(c) an amount of an organic phosphite ester effective to impart both anti-wear and friction modification to the composition, said organic phosphite ester having the formula:



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wherein R_1 and R_2, independently, represent the same or different C_{12}-C_{24} saturated or unsaturated, straight or branched chain hydrocarbyl radical having at most two unsaturated linkages.

32. The use according to claim 31, wherein said additive composition further comprises a dispersing amount of borated, aminated dispersant material comprising the reaction product of (i) the reaction product of (a) hydrocarbyl-substituted dicarboxylic acid material having a functionality of about 0.5 to about 2.8 and being derived from polyolefin having a number average molecular weight of from about 700 to about 5,000 reacted with monounsaturated C_4 to C_{10} dicarboxylic acid material wherein the carboxyl groups are located on adjacent carbon atoms and at least one of said carbon atoms is part of said monounsaturation, and (b) polyamine; and (ii) borating agent selected from at least one member of the group consisting of boric oxide, boron halide, metaborate, boric acid, mono-, di-, and trialkyl borate.