

Description

This invention relates to lubricants based on hydrotreated lubricating oils, and, more particularly, to multipurpose industrial oils for use in gear, hydraulic and other specialty applications. In its broadest sense, the invention relates to lubricating compositions comprising a major amount of a hydrotreated mineral lubricating oil and a minor amount of the combination of a fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation, and a sulfurized aliphatic olefinic compound containing from about 3—20 carbon atoms.

A wide variety of lubricant base oil stocks has been described in the prior art for preparing lubricating compositions. These include natural as well as synthetic oils. Natural oils include liquid petroleum oils and solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also are useful base oils. More recently, lubricant based stocks prepared by a hydrotreating process have been suggested as having advantages over solvent-extracted oils because the hydrotreating process is capable of producing new types of oils having modified structural and improved viscosimetric properties.

It is well known that the high pressure which occurs in certain types of gears and bearings may cause rupture of lubricant films with consequent damage to the machinery. Because of the severe conditions under which they are used, industrial and gear lubricants ordinarily must contain additives which maximize their capability of functioning under extreme pressure conditions. It has been suggested that certain compounds of metal-reactive elements, such as compounds of chlorine, sulfur, phosphorus and lead impart extreme pressure properties to various lubricants. Among the various compositions known to serve this purpose are various phosphorus- and sulfur-containing compositions, chiefly salts and esters of dialkylphosphorodithioic acids, and sulfurization products of various aliphatic olefinic compounds. These two types of compositions have been used in combination in lubricants of this type, and they serve to increase the effectiveness of the lubricant under conditions of extreme pressure.

Many of the known sulfurization products of olefinic compounds contain substantial amounts of active sulfur. The presence of active sulfur in a lubricant often has deleterious side effects such as staining of copper parts, increased wear on the metal components being lubricated, and a decrease in extreme pressure properties with the passage of time.

Various compositions prepared by the sulfurization of olefins have been described in the prior art as being useful in lubricant compositions. For example, U.S. Patent 4,191,659 describes the preparation of sulfurized olefinic compositions by the catalytic reaction of sulfur and hydrogen sulfide with olefinic compounds containing from 3 to 30 carbon atoms. Such compounds are reported to be useful in lubricating compositions, particularly those prepared for use as industrial gear lubricants.

US Patent No. 3966623 describes lubricating compositions containing a synergistic corrosion-inhibiting combination of 2,5-bis-hydrocarbyldithio-1,3,4-thiadiazole and a primary alkyl or alkenyl amine salt of 2-mercaptobenzo-thiazole. These compositions may also contain other additives including *inter alia* Na₂S-sulfurized diisobutylene and prime lard oil. Compositions comprising a hydrotreated lubricating oil are not disclosed in US Patent 3966623.

US Patent No. 2830956 describes hydraulic power transmission fluids, particularly oil compositions, containing a number of diverse additives including *inter alia* sulfurized or unsulfurized fatty oils such as sulfurized sperm oil or sulfurized lard oil. The use of a combination of sulfurized and unsulfurized fatty oils is also mentioned. Compositions comprising a hydrotreated lubricating oil are not disclosed in US Patent No. 2830956.

According to the present invention, there is provided a lubricating composition comprising:
a major amount of (A) a hydrotreated lubricating oil, and
a minor amount of the combination of:

(B) at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation;
and

(C) a sulfurization product of at least one aliphatic olefinic compound containing from about 3—20 carbon atoms which has been prepared by reaction with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.

In a preferred embodiment, the weight ratio of component (B) to component (C) is no greater than 1:1.

Such lubricant compositions derived from hydrotreated oils exhibit improved clarity, stability, extreme pressure properties, anti-wear capabilities and reduced staining of copper parts.

The compositions of the invention which are described more fully below comprise at least three components;

Component (A) comprising a major amount of the composition is a hydrotreated mineral lubricating oil;

Component (B) is at least one fatty acid ester of glycerol, and Component (C) is the sulfurization product of at least one aliphatic olefinic hydrocarbon containing from about 3 to 20 carbon atoms.

Component (A) in the compositions of the invention is a hydrotreated lubricating oil. Hydrotreating is a process for treating various oil stocks wherein an oil stock feed is combined with hydrogen and passed over a catalyst at elevated temperature and pressure. The extent of the treatment depends on the type of feedstock, the type of catalyst and the treating conditions. In the process, the hydrogen reacts with sulfur-

containing compounds in the oil to form hydrogen sulfide and saturated hydrocarbons. The hydrogen also reacts with nitrogen-bearing compounds in the oil to form ammonia. Thus, hydrotreating is particularly useful for crude oils containing undesirable amounts of sulfur and nitrogen. Hydrotreating of oil feedstocks also results in improved color, neutralization, and some reduction in carbon residue.

Hydrotreating can be classified into two types depending on the desired results and intended use. The hydrotreated stock may be used as feedstock for subsequent further processing, or the hydrotreated stock may be used as a base or blending stock for finished lubricants.

Hydrotreated oils of various types and viscosities are available from a variety of commercial sources since the process is used by most of the major oil refiners. Hydrotreated oil is desirable because of the reduction in undesirable sulfur and nitrogen content, improved color, improved stability and the relatively higher viscosity and natural viscosity index exhibited by such oils as compared to solvent refined oils. One of the difficulties in using hydrotreated oil is that many chemical additives normally used in lubricating oils are not compatible with the hydrotreated oils and thus cannot be used.

One group of hydrotreated oils is available from Gulf Canada under the general trade designation Paraflex. Particular oils are identified according to the ISO viscosity number which corresponds to the viscosity of the oil in centistokes at 40°C. Examples of such oils include Paraflex 10, Paraflex 100, Paraflex 460 (bright stock) and Paraflex 1000 (cylinder stock).

Component (B) in the compositions of the invention is at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation. The term "fatty acid" as used herein refers to acids which may be obtained by hydrolysis of naturally occurring vegetable or animal fats or oils. These fatty acids usually contain from 16 to 20 carbon atoms and are mixtures of saturated and unsaturated fatty acids. The unsaturated fatty acids generally contained in the naturally occurring vegetable or animal fats and oils may contain one or more double bonds and such acids include palmitoleic acid, oleic acid, linoleic acid, linolenic acid, petroselinic acid, erucic acid, gadoleic acid, vaccenic acid, ricinoleic acid and minor amounts of compounds containing more than 20 carbon atoms such as behenic acid.

The unsaturated fatty acid moiety of the esters useful as component (B) may be derived for example from the mixtures of acids (or derivatives thereof) present in tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil, or wheat germ oil. Tall oil is a mixture of rosin acids, mainly abietic acid, and unsaturated fatty acids, mainly oleic and linoleic acids. Tall oil is a by-product of the sulfate process for the manufacture of wood pulp.

The compounds useful as component (B) in the compositions of the invention are fatty acid esters of glycerol which contain olefinic unsaturation in the fatty acid moiety. Of these, the most particularly preferred are the fatty oils, that is, naturally occurring esters of glycerol with the fatty acids described above, and synthetic esters of similar structure. Examples of naturally occurring fats and oils containing unsaturation include animal fats such as neat's-foot oil, lard oil, depot fat, beef tallow, etc. Examples of naturally occurring vegetable oils useful as component (B) include cottonseed oil, corn oil, poppy-seed oil, safflower oil, sesame oil, soybean oil, sunflower seed oil and wheat germ oil.

The fatty acid esters which are useful as component (B) in the invention also may be prepared from aliphatic olefinic acids of the type described above such as oleic acid, linoleic acid, linolenic acid, and behenic acid by reaction with glycerol.

Component (C) in the compositions of this invention is a sulfurization product of at least one aliphatic olefinic hydrocarbon compound containing about 3—20 carbon atoms. The olefinic compounds which may be sulfurized to form component (C) are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula $R^1R^2C=CR^3R^4$, wherein each of R^1 , R^2 , R^3 and R^4 is hydrogen or an organic radical. In general, the R values in the above formula which are not hydrogen may be satisfied by such groups as $-R^5$, $-C(R^5)_3$, $-COOR^5$, $-CON(R^5)_2$, $-COON(R^5)_2$, $-COOM$, $-CN$, $-C(R^5)=NR^5$, $-X$ or $-YR^5$, wherein:

each R^5 is independently hydrogen, alkyl, alkenyl, aryl, alkylaryl, substituted alkyl or substituted alkenyl, with the proviso that any two R^5 groups can be alkylene or substituted alkylene whereby a ring of up to about 12 carbon atoms is formed;

M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium);

X is halogen (e.g., chloro, bromo, or iodo); and

Y is oxygen or divalent sulfur.

The nature of the substituents in the substituted moieties described above is not normally a critical aspect of the invention and any such substituent is useful so long as it is or can be made compatible with lubricating environments and does not interfere under the contemplated reaction conditions. Thus, substituted compounds which are so unstable as to deleteriously decompose under the reaction conditions employed are not contemplated. However, certain substituents such as keto or aldehyde can desirably undergo sulfurization. The selection of suitable substituents is within the skill of the art or may be established through routine testing. Typical of such substituents include any of the above-listed moieties as well as hydroxy, carboxy, carbalkoxy, amidine, amino, sulfonyl, sulfinyl, sulfonate, nitro, phosphate, phosphite, alkali metal mercapto and the like.

The olefinic compound is usually one in which each R group which is not hydrogen is independently

alkyl or alkenyl, or (less often) a corresponding substituted radical. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R³ and R⁴ are hydrogen and R¹ and R² are alkyl (that is, the olefin is aliphatic).

Propylene, isobutene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutene and diisobutene are particularly desirable because of their availability and the particularly high sulfur-containing compositions which can be prepared therefrom.

The sulfurizing reagent used for the preparation of component (C) is a mixture of hydrogen sulfide and sulfur.

The amounts of sulfur and hydrogen sulfide per mole of olefinic compound are, respectively, usually about 0.3—3.0 gram-atoms and about 0.1—1.5 moles. The preferred ranges are about 0.5—2.0 gram-atoms and about 0.4—1.25 moles respectively, and the most desirable ranges are about 0.8—1.8 gram-atoms and about 0.4—0.8 mole respectively.

The temperature range in which the sulfurization reaction is carried out is generally about 50—350°C. The preferred range is about 100—200°C, with about 125—180°C. being especially suitable. The reaction is often preferably conducted under superatmospheric pressure; this may be and usually is autogenous pressure (i.e., the pressure which naturally develops during the course of the reaction) but may also be externally applied pressure. The exact pressure developed during the reaction is dependent upon such factors as the design and operation of the system, the reaction temperature, and the vapor pressure of the reactants and products and it may vary during the course of the reaction.

The sulfurization reaction is effected in the presence of a sulfurization catalyst. These materials may be acidic, basic or neutral, but are preferably basic materials, especially nitrogen bases including ammonia and amines. The amount of catalyst used is generally about 0.05—2.0% of the weight of the olefinic compound. In the case of the preferred ammonia and amine catalysts, about 0.0005—0.5 mole per mole of olefin is preferred, and about 0.001—0.1 mole is especially desirable.

Following the preparation of the sulfurized mixture, it is preferred to remove substantially all low boiling materials, typically by venting the reaction vessel or by distillation at atmospheric pressure, vacuum distillation or stripping, or passage of an inert gas such as nitrogen through the mixture at a suitable temperature and pressure.

A further optional step in the preparation of component (C) is the treatment of the sulfurized product, obtained as described hereinabove, to reduce active sulfur. An illustrative method is treatment with an alkali metal sulfide as described in U.S. Patent 3,498,915. Other optional treatments may be employed to remove insoluble by-products and improve such qualities as the odor, color and staining characteristics of the sulfurized compositions.

U.S. Patent 4,119,549 discloses suitable sulfurization products useful as component (C). Several specific sulfurized compositions are described in the working examples thereof. The following example illustrates the preparation of one such composition.

Example 1

Sulfur (629 parts, 19.6 moles) is charged to a jacketed high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 800 Pa (6 torr) and cooling, 1100 parts (19.6 moles) of isobutene, 334 parts (9.8 moles) of hydrogen sulfide and 7 parts of n-butylamine are charged to the reactor. The reactor is heated using steam in the external jacket, to a temperature of about 171°C, over about 1.5 hours. A maximum pressure of 5 MPa (720 psig) is reached at about 138°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 4.75 hours at about 171°C, the unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid.

As mentioned above, the sulfurizing agent may be sulfur, and the reaction is effected by heating the olefinic compound with sulfur at a temperature of from 100—250°C, usually about 150—210°C with efficient agitation and in an inert atmosphere (e.g., nitrogen). The weight ratio of olefin to sulfur may be as high as 15:1 and is generally between about 5:1 and 10:1.

It is frequently advantageous to add the sulfur portionwise to the olefin. While it is usually preferred that the reaction mixture consist entirely of the olefin and sulfur, the reaction may be effected in the presence of an inert solvent such as alcohol, ether, ester, aliphatic hydrocarbon or halogenated aromatic hydrocarbon which is a liquid at the reaction temperatures employed.

Following the reaction, insoluble by-products may be removed by filtration, usually at an elevated temperature (about 80—120°C). The filtrate is the desired sulfurized product.

The compositions of this invention typically contain components (B) and (C) in a weight ratio no greater than 1:1. Generally, the weight ratio of component (B) to component (C) is from about 0.2:1 to about 1:1, and more preferably, from about 0.2:1 to about 0.5:1. The following examples are illustrative of combinations of components (B) and (C) which are useful in the invention.

TABLE I

Ingredient	Example	Parts by weight	
		2	3
Soybean oil			0.25
Cottonseed oil		0.20	
Product of Example 1		0.40	0.62

The lubricating compositions of this invention comprise a major amount of component (A) and a minor amount, generally from about 0.01 to 20% and preferably from about 0.01 to 10%, by weight of component (A) of the combination of components (B) and (C). The lubricating compositions of the invention may be prepared merely by blending the oil and the components, or the components may be diluted in substantially inert diluents and thereafter blended with the hydrotreated oil. The diluent, if any, may be the oil used as a lubricant base and may include other additives such as those described hereinafter.

As previously indicated, the compositions of this invention are useful as industrial and gear lubricants. The lubricants provide longer lasting extreme pressure properties, anti-wear capability and reduced staining of copper parts. The lubricants of the invention can be used as crankcase lubricating oils for spark ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. Automatic transmission fluids, transaxle lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions can be prepared using the lubricant compositions of the present invention.

The lubricants of this invention based on hydrotreated oil may contain small amounts of synthetic oils and natural oils refined by other methods. Generally, however, there is little advantage in using oil which is not hydrotreated. Natural oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins [e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes) and mixtures thereof, etc.]; alkylbenzenes [e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes, etc.]; polyphenyls [e.g., biphenyls, terphenyls, alkylated polyphenols, etc.]; alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500—1000, diethyl ether of polypropylene glycol having a molecular weight of 1000—1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters; mixed C₃—C₈ fatty acid esters or the C₁₃ Oxo acid diester of tetraethylene glycol.

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

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

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; [e.g., tetraethyl silicate, tetraisopropyl silicate, tetra(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxyl)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, etc.]. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g. tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid, etc.) and polymeric tetrahydrofurans and the like.

Small amounts of unrefined, refined and re-refined oils (and mixtures of each with each other) of the type disclosed hereinabove can be included in the lubricant composition of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without

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

Generally, the lubricants of the present invention contain an amount of the combination of components (A) and (B) sufficient to provide extreme pressure and anti-wear properties. Normally this amount will be about 0.01 to about 20%, preferably about 0.01 to about 10% of the total weight of the hydrorefined oil, component (A).

The invention also contemplates the use of other additives in the lubricating compositions of this invention. Such additives include, for example, detergents and dispersants of the ash-producing or ashless type, corrosion- and oxidation-inhibiting agents, pour point depressing agents, auxiliary extreme pressure agents, color stabilizers and anti-foam agents.

The ash-producing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acid, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature above 50°C and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at elevated temperatures such as 60—200°C.

Ashless detergents and dispersants are so called despite the fact that, depending on its constitution, the dispersant may upon combustion yield a non-volatile material such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen-containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. Patents including the following:

3,163,603	3,351,552	3,541,012
3,184,474	3,381,022	3,542,678
3,215,707	3,399,141	3,542,680
3,219,666	3,415,750	3,567,637
3,271,310	3,433,744	3,574,101
3,272,746	3,444,170	3,576,743
3,281,357	3,448,048	3,630,904
3,306,908	3,448,049	3,632,510
3,311,558	3,451,933	3,632,511
3,316,177	3,454,607	3,697,428
3,340,281	3,467,668	3,725,441
3,341,542	3,501,405	4,234,435
3,346,493	3,522,179	Re 26,433

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably polyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. Patents:

3,275,554	3,454,555
3,438,757	3,565,804

(3) Reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. Patents are illustrative:

5	2,459,112	3,442,808	3,591,598
	2,962,442	3,448,047	3,600,372
	2,984,550	3,454,497	3,634,515
	3,036,003	3,459,661	3,649,229
	3,166,516	3,461,172	3,697,574
10	3,236,770	3,493,520	3,725,277
	3,355,270	3,539,633	3,725,480
	3,368,972	3,558,743	3,726,882
	3,413,347	3,586,629	3,980,569

15 (4) Products obtained by post-treating the carboxylic amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents:

20	3,036,003	3,282,955	3,493,520	3,639,242
	3,087,936	3,312,619	3,502,677	3,649,229
	3,200,107	3,366,569	3,513,093	3,649,659
	3,216,936	3,367,943	3,533,945	3,658,836
	3,254,025	3,373,111	3,539,633	3,697,574
25	3,256,185	3,403,102	3,573,010	3,702,757
	3,278,550	3,442,808	3,579,450	3,703,536
	3,280,234	3,455,831	3,591,598	3,704,308
	3,281,428	3,455,832	3,600,372	3,708,522

30 (5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. Patents:

35	3,329,658	3,666,730
	3,449,250	3,687,849
	3,519,565	3,702,300

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents are exemplified by 40 chlorinated aliphatic hydrocarbons such as chlorinated wax; aromatic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, bis-(chlorobenzyl)disulfide and sulfurized alkylphenol; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl 45 phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, di-isobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)phosphorodithioate, cadmium 50 dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Components (B) and (C) can be added directly to the hydrorefined oil. Preferably, however, they are 55 diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain about 20—90% by weight of the combination of components (A) and (B) such as the compositions of Examples 2 and 3 and may contain, in addition, one or more other additives known in the art or described hereinabove.

60 Illustrative lubricants of this invention comprise principally a hydrorefined mineral oil in combination with about 0.1 to 10% by weight or more of the combinations of Examples 2 and 3 and with other known lubricant additives. The following specific examples in Table II illustrate lubricating compositions according to the invention. The lubricants of Examples 4—6 are prepared from concentrates of the indicated additives in a diluent oil.

The lubricants of Examples 4 and 5 are prepared by blending 98 parts of the hydrorefined oil with 2 parts of concentrate, and Example 6 is prepared by blending 97 parts of hydrorefined oil with 3 parts of the concentrate.

TABLE II

	Example	Parts by weight		
		4	5	6
5	Hydrotreated oil*	98.00	98.00	97.00
	Combination of Example 3	0.187	0.865	1.312
	Amine-neutralized phosphate ester of hydroxyalkyl dialkylphosphorodithioate	—	0.40	0.60
10	Alkyl acrylate-dialkylphosphorodithioic acid adduct	0.40	—	—
	Hydroxypropyl tetrapropenyl succinate	0.06	—	—
	Polyoxyalkylene demulsifier	0.005	0.005	0.008
	N-tridecyltrimethylenediamine	0.05	0.05	0.08
15	Tolyltriazole	0.015	0.015	0.022
	Silicone anti-foam agent	0.02	0.02	0.03
	Diluent oil	0.58	0.645	0.968

* a hydrotreated bright stock: $\eta_{sp}/c = 102$; viscosity of 466.0 cst at 40°C. and 32.61 at 100°C.

Claims

1. A lubricating composition comprising:
a major amount of (A) a hydrotreated lubricating oil, and
a minor amount of the combination of:
(B) at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation;
and
(C) a sulfurization product of at least one aliphatic olefinic compound containing from about 3—20 carbon atoms which has been prepared by reaction with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.
2. A composition according to Claim 1 wherein component (B) is at least one vegetable oil.
3. A composition according to Claim 2 wherein component (B) is soybean oil.
4. A composition according to any preceding claim wherein the weight ratio of component (B) to component (C) is no greater than 1:1.
5. A composition according to Claim 4 wherein the weight ratio of component B to component C is from about 0.2:1 to 0.5:1.
6. A composition according to any preceding claim wherein component (C) is a sulfurization product of at least one of propylene, isobutene and dimers, trimers and tetramers thereof.
7. A composition according to Claim 6 wherein component (C) has been prepared by reacting isobutene with a mixture of sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.
8. A composition according to any preceding claim wherein the sulfurization catalyst is a basic catalyst.
9. A composition according to Claim 9 wherein the catalyst is n-butylamine.
10. A lubricating composition comprising:
a major amount of (A) a hydrotreated lubricating oil, and
about 0.01 to 10% by weight of the combination of:
(B) soybean oil, and
(C) the sulfurization product of at least one of propylene, isobutene and dimers, trimers and tetramers thereof which has been prepared by reacting with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst;
the weight ratio of component B to component C being no greater than 1:1.
11. A method for preparing a lubricating composition comprising admixing:
a major amount of (A) a hydrotreated lubricating oil, and
a minor amount of the combination of:
(B) at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation;
and
(C) a sulfurization product of at least one aliphatic olefinic compound containing from about 3—20 carbon atoms which has been prepared by reacting with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.

Patentansprüche

1. Schmiermittel umfassend:
eine größere Menge von (A) einem hydrotreatierten Schmieröl, und
eine kleinere Menge einer Kombination von

TABLE II

	Example	Parts by weight		
		4	5	6
5	Hydrotreated oil*	98.00	98.00	97.00
	Combination of Example 3	0187	0.865	1.312
	Amine-neutralized phosphate ester of hydroxyalkyl dialkylphosphorodithioate	—	0.40	0.60
10	Alkyl acrylate-dialkylphosphorodithioic acid adduct	0.40	—	—
	Hydroxypropyl tetrapropenyl succinate	0.06	—	—
	Polyoxyalkylene demulsifier	0.005	0.005	0.008
	N-tridecyltrimethylenediamine	0.05	0.05	0.08
15	Tolyltriazole	0.015	0.015	0.022
	Silicone anti-foam agent	0.02	0.02	0.03
	Diluent oil	0.58	0.645	0.968

* a hydrotreated bright stock: VI=102; viscosity of 466.0 cst at 40°C. and 32.61 at 100°C.

Claims

1. A lubricating composition comprising:
a major amount of (A) a hydrotreated lubricating oil, and
a minor amount of the combination of:
(B) at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation;
and
(C) a sulfurization product of at least one aliphatic olefinic compound containing from about 3—20 carbon atoms which has been prepared by reaction with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.
2. A composition according to Claim 1 wherein component (B) is at least one vegetable oil.
3. A composition according to Claim 2 wherein component (B) is soybean oil.
4. A composition according to any preceding claim wherein the weight ratio of component (B) to component (C) is no greater than 1:1.
5. A composition according to Claim 4 wherein the weight ratio of component B to component C is from about 0.2:1 to 0.5:1.
6. A composition according to any preceding claim wherein component (C) is a sulfurization product of at least one of propylene, isobutene and dimers, trimers and tetramers thereof.
7. A composition according to Claim 6 wherein component (C) has been prepared by reacting isobutene with a mixture of sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.
8. A composition according to any preceding claim wherein the sulfurization catalyst is a basic catalyst.
9. A composition according to Claim 9 wherein the catalyst is n-butylamine.
10. A lubricating composition comprising:
a major amount of (A) a hydrotreated lubricating oil, and
about 0.01 to 10% by weight of the combination of:
(B) soybean oil, and
(C) the sulfurization product of at least one of propylene, isobutene and dimers, trimers and tetramers thereof which has been prepared by reacting with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst;
the weight ratio of component B to component C being no greater than 1:1.
11. A method for preparing a lubricating composition comprising admixing:
a major amount of (A) a hydrotreated lubricating oil, and
a minor amount of the combination of:
(B) at least one fatty acid ester of glycerol wherein the fatty acid moiety contains olefinic unsaturation;
and
(C) a sulfurization product of at least one aliphatic olefinic compound containing from about 3—20 carbon atoms which has been prepared by reacting with elemental sulfur and hydrogen sulfide in the presence of a sulfurization catalyst.

Patentansprüche

1. Schmiermittel umfassend:
eine größere Menge von (A) einem hydrotreatierten Schmieröl, und
eine kleinere Menge einer Kombination von



(B) mindestens einem Fettsäureester von Glycerin, in dem die Fettsäureeinheit olefinisch ungesättigte Bindungen aufweist; und

(C) ein Sulfurierungsprodukt von mindestens einer aliphatischen olefinischen Verbindung mit etwa 3 bis 20 Kohlenstoffatomen, das durch Umsetzung mit elementarem Schwefel und Schwefelwasserstoff in Gegenwart eines Sulfurierungskatalysators hergestellt worden ist.

2. Mittel nach Anspruch 1, in dem die Komponente (B) mindestens ein pflanzliches Öl ist.

3. Mittel nach Anspruch 2, in dem die Komponente (B) Sojabohnenöl ist.

4. Mittel nach einem der vorangehenden Ansprüche, in dem das Gewichtsverhältnis von Komponente (B) zu Komponente (C) nicht größer als 1:1 ist.

5. Mittel nach Anspruch 4, in dem das Gewichtsverhältnis von Komponente (B) zu Komponente (C) etwa 0,2:1 bis 0,5:1 beträgt.

6. Mittel nach einem der vorangehenden Ansprüche, in dem die Komponente (C) ein Sulfurierungsprodukt mindestens einer der Verbindungen Propylen, Isobutylen und Dimeren, Trimeren und Tetrameren davon ist.

7. Mittel nach Anspruch 6, in dem die Komponente (C) durch Umsetzung von Isobuten mit einem Gemisch aus Schwefel und Schwefelwasserstoff in Gegenwart eines Sulfurierungskatalysators hergestellt worden ist.

8. Mittel nach einem der vorangehenden Ansprüche, in dem der Sulfurierungskatalysator ein basischer Katalysator ist.

9. Mittel nach Anspruch 9, in dem der Katalysator n-Butylamin ist.

10. Schmiermittel, umfassend:

eine größere Menge von (A) einem hydorraffinierten Schmieröl, und etwa 0,01 bis 10 Gew.-% einer Kombination aus:

(B) Sojabohnenöl, und

(C) einem Sulfurierungsprodukt von mindestens einer der Verbindungen Propylen, Isobutylen und Dimeren, Trimeren und Tetrameren davon, das durch Umsetzung mit elementarem Schwefel und Schwefelwasserstoff in Gegenwart eines Sulfurierungskatalysators hergestellt worden ist, wobei das Gewichtsverhältnis von Komponente (B) zu Komponente (C) nicht größer als 1:1 ist.

11. Verfahren zur Herstellung eines Schmiermittels, umfassend das Vermischen von:

einer größeren Menge von (A) einem hydorraffinierten Schmieröl, und

einer kleineren Menge einer Kombination aus:

(B) mindestens einem Fettsäureester von Glycerin, in dem die Fettsäureeinheit olefinisch ungesättigte Bindungen enthält, und

(C) einem Sulfurierungsprodukt mindestens einer aliphatischen olefinischen Verbindung, die etwa 3 bis 20 Kohlenstoffatome enthält, das durch Umsetzung mit elementarem Schwefel und Schwefelwasserstoff in Gegenwart eines Sulfurierungskatalysators hergestellt worden ist.

Revendications

1. Une composition lubrifiante comprenant:

Une quantité prépondérante de (A) une huile lubrifiante hydorraffinée, et une petite quantité de la combinaison de:

(B) au moins un ester d'acide gras du glycérol, dans lequel la partie acide gras contient une insaturation oléfinique; et

(C) un produit de sulfuration d'au moins un composé aliphatique oléfinique renfermant environ de 3 à 20 atomes de carbone, qui a été préparé par réaction avec du soufre élémentaire et du sulfure d'hydrogène en présence d'un catalyseur de sulfuration.

2. Une composition selon la revendication 1, dans laquelle le composant (B) est au moins une huile végétale.

3. Une composition selon la revendication 2, dans laquelle le composant (B) est de l'huile de soja.

4. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le rapport pondéral du composant (B) au composant (C) n'est pas supérieure à 1:1.

5. Une composition selon la revendication 4, dans laquelle le rapport pondéral du composant (B) au composant (C) est d'environ 0,2:1 à 0,5:1.

6. Une composition selon l'une des revendications précédentes, dans laquelle le composant (C) est un produit de sulfuration d'au moins un composé parmi le propylène, l'isobutylène et leurs dimères, trimères et tétramères.

7. Une composition selon la revendication 6, dans laquelle le composant (C) a été préparé en faisant réagir de l'isobutène avec un mélange de soufre et d'hydrogène sulfuré en présence d'un catalyseur de sulfuration.

8. Une composition selon une des revendications précédentes, dans laquelle le catalyseur de sulfuration est un catalyseur basique.

9. Une composition selon la revendication 8, dans laquelle le catalyseur est la n-butylamine.

10. Une composition lubrifiante comprenant:

une quantité prépondérante de (A) une huile lubrifiante hydorraffinée, et



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environ 0,01 à 10% en poids de la combinaison de:
(B) une huile de soja, et

(C) le produit de sulfuration, d'au moins l'un des composés polypropylène, isobutylène, et leurs dimères, trimères et tétramères, qui a été préparé par réaction avec du soufre élémentaire et du sulfure d'hydrogène en présence d'un catalyseur de sulfuration:

le rapport pondéral du composé (B) au composant (C) n'étant pas supérieur à 1:1.

11. Une méthode pour préparer une composition lubrifiante, comportant le mélange:
d'une quantité prépondérante de (A) une huile lubrifiante hydrraffinée, et
une petite quantité de la combinaison de:

(B) au moins un ester d'acide gras du glycérol, dans lequel la partie acide gras renferme une insaturation oléfinique; et

(C) un produit de sulfuration d'au moins un composé aliphatique oléfinique renfermant d'environ 3 à 20 atomes de carbone, qui a été préparé par réaction avec du soufre élémentaire et du sulfure d'hydrogène en présence d'un catalyseur de sulfuration.

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