(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 051 998**
B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **10.04.85**

(21) Application number: **81305297.4**

(22) Date of filing: **06.11.81**

(51) Int. Cl.^{4}: **C 10 M 141/10,**
C 10 M 129/76,
C 10 M 149/12

(54) **Lubricating oil composition.**

(30) Priority: **10.11.80 US 205314**

(43) Date of publication of application:
19.05.82 Bulletin 82/20

(45) Publication of the grant of the patent:
10.04.85 Bulletin 85/15

(84) Designated Contracting States:
DE FR GB IT NL

(56) References cited:
GB-A-1 055 337
US-A-4 105 571

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EP 0 051 998 B1

Courier Press, Leamington Spa, England.

Description

This invention relates to a storage stable lubricating oil composition having improved anti-friction properties.

There has been considerable effort in recent years to develop lubricating oil compositions which will reduce friction in engines and particularly automotive engines. This effort is based on the need to improve the fuel economy of such engines which operate on petroleum fuel, a product having a declining source of supply and an escalating price. It is known that high engine friction causes significant energy loss and thus one way to improve fuel economy is to reduce such friction.

Known ways to solve the problem of energy losses due to high friction e.g., in crankcase motor oils include the use of synthetic ester base oils which are expensive and the use of insoluble molybdenum sulfides which have the disadvantage of giving the oil composition a black or hazy appearance.

Another approach to reduce energy losses by the use of a lubricating oil composition involves a composition containing an additive combination of an oil soluble friction reducing ester component derived from esterification of a polycarboxylic acid with a glycol and a zinc dihydrocarbyl dithiophosphate. This type of composition is disclosed in U.S. Patent 4,105,571 which notes that while a lubricating composition containing the additive packages of such ester and zinc thiophosphate components provides excellent anti-friction and anti-wear properties, it presents compatibility and stability problems. The problem is solved by adding a selected ashless dispersant containing a high molecular weight aliphatic hydrocarbon oil solubilizing group attached thereto to the composition, and preferably predispersing either the ester and/or zinc thiophosphate components prior to their addition to the remainder of the composition. Such ashless dispersants may contain hydroxyl groups as noted in the patent.

While the above approaches all provide reduced engine friction and consequently improved fuel economy, there is always the need and desire for further reductions in energy losses due to friction or otherwise since even small reductions per engine can result in a rather large saving in fuel, particularly when considering the total number of engines in use.

Summary of the Invention

It has now surprisingly been discovered that lubricating oil compositions containing an additive combination of an ester of a polycarboxylic acid and a glycol or glycerol plus zinc dihydrocarbyl dithiophosphate can be made storage stable and have particularly improved friction reducing properties when an ashless dispersant containing a selected amount of free hydroxyl is used. More particularly a storage stable lubricating oil composition with improved friction reducing properties is provided by the composition of this invention which includes an additive combination of (1) an ester of a polycarboxylic acid with a glycol or glycerol (2) a zinc dihydrocarbyl dithiophosphate and (3) an ashless dispersant containing a high molecular weight aliphatic hydrocarbon oil solubilizing group attached thereto and a selected amount of free hydroxyl groups.

In accordance with the present invention a storage stable lubricating oil composition with improved friction reducing properties is provided by a composition comprising a major portion of lubricating oil, from about 0.01 to 1.0 parts by weight of an ester of a polycarboxylic acid with a glycol or glycerol, from 0.01 to 5.0 parts by weight of zinc dihydrocarbyl dithiophosphate and from 0.1 to 20 parts by weight of an hydroxyl containing ashless dispersant having a high molecular weight aliphatic hydrocarbon oil solubilizing group attached thereto, said dispersant containing from 0.35 to 1.8 millimoles (mM) of free hydroxyl per gram of dispersant, all weights based on 100 parts by weight of said lubricating oil composition.

Detailed Description of the Invention

As previously indicated the present invention relates to a storage stable lubricating oil composition having particularly improved friction reducing properties comprising an additive combination of an ester of a polycarboxylic acid and a glycol or glycerol, zinc dihydrocarbyl dithiophosphate and an ashless dispersant containing a selected amount of free hydroxyl groups.

The oil soluble friction reducing ester component used in the composition of this invention generally, can be any hydroxy substituted oil soluble ester of a polycarboxylic acid.

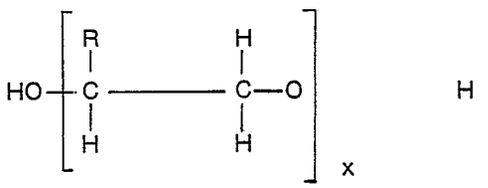
Best results are, however, obtained when such compounds are derived from the esterification of a polycarboxylic acid with a glycol or glycerol, preferably glycol. Such an ester may be a partial, di- or polyester with typical formulas of the ester represented by the following general formulas when using a glycol:

(1) HO—R—OOC—R″—COOH
(2) HO—R—OOC—R″—COOR′—OH
(3) HO—R—OOC—R″—COOR—OOC—R″—COOR′—OH

wherein R″ is the hydrocarbon radical of said acid and each R and R′ may be the same or different hydrocarbon radicals associated with a glycol or diol as hereinafter defined. It will, of course, be appreciated that esters of the type illustrated by the foregoing formulas can be obtained by esterifying a polycarboxylic acid, or a mixture of such acids, with a diol or mixture of such diols.

The polycarboxylic acid used in preparing the ester may be an aliphatic saturated or unsaturated acid and will generally have a total of about 24 to about 90, preferably about 24 to about 60 carbon atoms and about 2 to about 4, preferably about 2 to about 3 and more preferably about 2 carboxylic acid groups with at least about 9 up to about 42 carbon atoms, preferably about 12 to about 42 and more preferably about 16 to about 22 carbon atoms between the carboxylic acid groups.

The oil insoluble glycol which is reacted with the polycarboxylic acid may be an alkane diol, i.e. alkylene glycol or an oxa-alkane diol, i.e. polyalkylene glycol, straight chain or branched. The alkane diol may have from about 2 to about 12 carbon atoms and preferably about 2 to about 5 carbon atoms in the molecule and the oxa-alkane diol will, generally, have from about 4 to about 200, preferably about 4 to about 100 carbon atoms. The oxa-alkane diol (polyalkylene glycol) will, of course, contain periodically repeating groups of the formula:



wherein R may be H, CH_3, C_2H_5 or C_3H_7, and x is 2 to 100, preferably 2 to 25. The preferred alkane diol or alkylene glycol is ethylene glycol and the preferred oxa-alkane diol or polyalkylene glycol is diethylene glycol. As indicated previously, glycerol may also be used in preparing the ester of polycarboxylic acid and it is contemplated that such component will also include its higher molecular weight analogues.

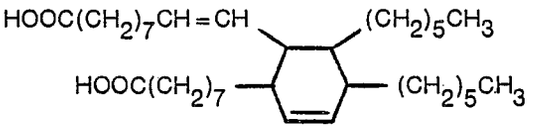
While any of the esters as set forth above can be effectively used, best results are, however, obtained with such compounds wherein the carboxyl groups of the polycarboxylic acid are separated from each other by from about 16 to about 22 carbon atoms and wherein the hydroxy groups are separated from the closest carboxyl group by from about 2 to about 12 carbon atoms. Particularly desirable results have been obtained with additives prepared by esterifying a dimer of a fatty acid particularly those containing conjugated unsaturation with a polyhydroxy compound. Such dimers are, of course, clearly taught in U.S. Patent 3,180,832 which was granted on April 27, 1965 and U.S. Patent 3,429,817 which was granted on February 25, 1969, and as there indicated, the hydrocarbon portion of the dimer or dicarboxylic acid thus obtained may contain a six member ring. The formation of the dimer from linoleic acid, oleic acid and mixtures of these acids is illustrated by the following:

A. $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH \xrightarrow[300°C]{\Delta}$

9,12 Linoleic Acid

$CH_3(CH_2)_5CH{=}CHCH{=}CH(CH_2)_7COOH \xrightarrow[\text{Diels-Alder}\ \Delta]{\text{2 molecules 9–11 acid}}$

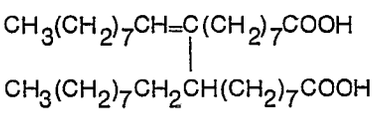
9,11 Linoleic Acid



Linoleic Acid Dimer (dilinoleic acid)

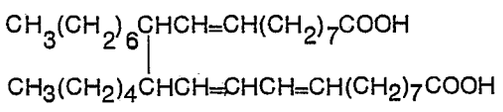
B. $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[\text{Diels Alder}\ \Delta]{\text{2 molecules oleic acid}}$

Oleic Acid



Oleic Acid Dimer (Dioleic Acid)

C. 9,11 Linoleic Acid + Oleic Acid $\xrightarrow[\Delta]{\text{Diels-Alder}}$

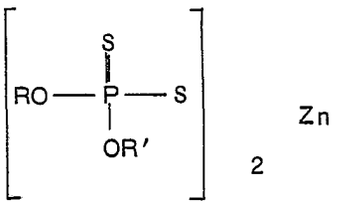


Mixed Dimer

It will, of course, be appreciated that while the reactions illustrated produce the dimers, commercial application of the reactions will, generally, lead to trimer formation and in some cases the product thus obtained will contain minor amounts of unreacted monomer or monomers. As a result, commercially available dimer acids may contain as much as 25% trimer and the use of such mixtures is within the scope of the present invention.

The preferred hydroxy-substituted ester lubricity additives useful in the present invention will be the reaction product of a dimerized fatty acid, such as those illustrated, and an oil insoluble glycol and may be produced by various techniques. As previously pointed out, the preferred acid dimers are the dimers of linoleic acid, oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specifically satisfactory glycols in addition to ethylene glycol and polyethylene glycol are, for example, propylene glycol, polypropylene glycol, butylene glycol, polybutylene glycol and the like.

The zinc dihydrocarbyl dithiophosphates useful in the present invention are salts of dihydrocarbyl esters of dithiophosphoric acids and may be represented by the following formula:



wherein R and R′ may be the same or different hydrocarbyl radicals containing from 1 to 18 and preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R′ groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, tert-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms in the dithiophosphoric acid will average about 5 or greater.

The zinc dihydrocarbyl dithiophosphates which are useful in the compositions of the present invention may be prepared in accordance with known techniques by first esterifying a dithiophosphoric acid usually by reaction of an alcohol or phenol with P_2S_5 and then neutralizing the dithiophosphoric acid ester with a suitable zinc compound such as zinc oxide. In general, the alcohol or mixtures of alcohols containing from 1 to 18 carbon atoms may be used to effect the esterification. The hydrocarbon portion of the alcohol may, for example, be a straight or branched chain alkyl or alkenyl group, or a cycloaliphatic or aromatic group. Among the alcohols which are generally preferred for use as starting materials in the preparation of the esters may be mentioned ethyl, isopropyl, amyl, 2-ethylhexyl, lauryl, stearyl and methyl cyclohexyl alcohols as well as commercial mixtures of alcohols, such as the mixture of alcohols derived from coconut oil and known as "Lorol B" alcohol, which mixture consists essentially of alcohols in the C_{10} to C_{18} range. Other natural products containing alcohols such as the alcohols derived from wool fat, natural waxes and the like may be used. Moreover, alcohols produced by the oxidation of petroleum hydrocarbon products as well as the Oxo-alcohols produced from olefins, carbon monoxide and hydrogen may be employed. Further aromatic compounds such as alkylated phenols of the type n-butyl phenol, tertiaryamyl phenol, diamyl phenol, tertiary octyl phenol, cetyl phenol, petroleum phenol and the like as well as the corresponding naphthols may be employed in like manner.

Following the esterification, the diester is then neutralized with a suitable basic zinc compound or a mixture of such compounds. In general, any compound could be used but the oxides, hydroxides and carbonates are most generally employed.

Generally, any lubricating oil ashless dispersant containing a high molecular weight aliphatic hydrocarbon oil solubilizing group attached thereto and the selected amount of free hydroxyl groups can be used in the composition of this invention. More particularly, said dispersant will contain from about 0.35 to about 1.8 millimoles of free hydroxyl per gram of dispersant, preferably from about 0.5 to about 1.5 and more preferably about 0.7 to about 1.3 millimoles of free hydroxyl per gram of dispersant. In referring to

dispersant in the context of free hydroxyl groups, the gram weight is of active dispersant, i.e. it does not include the carrier or lubricating oil in which the dispersant is diluted or otherwise dispersed.

The significance of the hydroxyl content in the dispersant is the essential feature of this invention since it has surprisingly been found that controlling hydroxyl content per gram of active dispersant results in significantly lower engine friction. Additionally, there is a minimum amount of hydroxyl content which must be maintained in the dispersant in order to retain composition stability. Accordingly, it is essential that the dispersant contain a selected amount of free hydroxyl content as described herein to provide a lubricating composition with improved friction reducing properties while retaining its stability.

A variety of compounds may be used as the ashless dispersant in the composition of this invention provided they have a suitable high molecular weight aliphatic hydrocarbon oil solubilizing group attached thereto and most important a selected amount of free hydroxyl groups. Dispersant compounds of this type include esters of mono and polycarboxylic acids with polyhydric alcohols, phenols and naphthols as well as nitrogen containing compounds containing the necessary hydroxyl content as previously noted. It is contemplated that mixtures and a wide variety of compounds may be utilized as the ashless dispersant or ashless dispersant system in this invention provided the necessary functionality is available, particularly the selected amount of free hydroxyl content. Thus, the ashless dispersant of this invention may comprise a mixture of a hydroxylated and non-hydroxylated compound provided the necessary functionality as defined herein is satisfied. Accordingly, the term ashless dispersant as used throughout this application is intended to include such mixtures and combination of compounds thereof.

The different dispersants which can be used in this invention are characterized by a long chain hydrocarbon group or groups, which may be attached, e.g. to the acid, so the acid contains a total of about 50 to about 400 carbon atoms, said acid being attached, e.g. to an amine and/or ester group or both.

Ester containing ashless dispersants of this invention can be derived from polyhydric aliphatic alcohols or polyhydric aromatic hydroxyl containing compounds such as phenols and naphthols. The polyhydric alcohols and aromatic compounds used will preferably contain from 2 to about 10 hydroxy radicals and are illustrated by ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other alkylene glycols in which the alkylene radicals contain from about 2 to about 8 carbon atoms. Also, resorcinol, catechol, p,p'-dihydroxybiphenyl, 4,4'-methylene bis-phenol, di (hydroxyphenyl) oxide, and di (hydroxyphenyl) sulfide. Other useful polyhydric compounds include glycerol, mono-oleate of glycerol, pentaerythritol, trimethylol propane, 9,10-dihydroxystearic acid, 1,2-butanediol, 2,3-hexanediol, 2,4 hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, and 1,2-cyclohexanediol. Carbohydrates such as sugars, starches, cellulose, etc., likewise may yield appropriate esters as exemplified by flucose, fructose, sucrose, rhamnose, mannose, glyceraldehyde, and galactose.

An especially preferred class of polyhydric alcohols are those having at least three hydroxy radicals, some of which have been esterified with a monocarboxylic acid having from about 8 to about 30 carbon atoms such as octanoic acid, oleic acid, stearic acid, linoleic acid, dodecanoic acid or tall oil acid. Examples of such partially esterified polyhydric alcohols are the mono-oleate of glycerol, monosterate of glycerol, didodecanote of erythritol.

The ester dispersant of this invention may also be derived from unsaturated alcohols, ether-alcohols, and amino alcohols including for example: oxy-alkylene, oxy-arylene, amino-alkylene, and amino-arylene substituted alcohols. Such compounds include di (hydroxyethyl) amine, tri (hydroxypropyl) amine, N,N,N,N-tetrahydroxytrimethylenediamine, 2-amino-2-methyl-1,3 propanediol, 2-amino-2-ethyl-1,3-propanediol, tris (hydroxymethyl) amino-methane, etc.

As indicated earlier, the particular dispersants used in this invention contain a long chain hydrocarbon group which will generally have about 50 to about 400 carbon atoms and preferably will be derived from an alkenyl succinic acid/anhydride where the alkenyl radical will have a molecular weight of at least about 900 and preferably at least about 1200 and more preferably at least about 1300.

A large number of dispersants having the above identified characteristics can be used in this invention some of which are disclosed in U.S. Patents 4,105,571; 3,542,678; 3,522,179; 3,542,680; 3,632,511; and 3,804,763. Methods for preparing such dispersants are generally well known and are also disclosed in the noted patents. Some particularly preferred dispersant combinations include 1) a combination of a polyisobutenyl succinic anhydride, a hydroxy compound e.g. pentaerythritol and a polyoxyalkylene polyamine e.g. polyoxypropylenediamine and a polyalkylene polyamine e.g. polyethylenediamine and tetraethylene pentamine and 2) a combination of polyisobutenyl succinic anhydride, polyalkylene polyamine e.g. tetraethylene pentamine and a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine e.g. pentaerythritol or trismethylolaminomethane.

In general, the zinc dihydrocarbyl dithiophosphate will be used in the lubricating composition at a concentration within the range of about 0.01 to about 5 parts by weight per 100 parts of lubricating oil composition and preferably from about 0.5 to about 1.5. The polycarboxylic acid/glycol or glycerol ester will be used at a concentration of about 0.01 to about 2.0, preferably about 0.05 to about 1.0 and more preferably 0.05 to 0.5 parts by weight per 100 parts of lubricating oil composition and the ashless dispersant will be employed at a concentration of about 0.1 to about 20 and preferably about 0.5 to about 10 parts by weight per 100 parts of lubricating oil composition.

The lubricating oil liquid hydrocarbons which may be used include the mineral lubricating oils and the

synthetic lubricating oils and mixtures thereof. The synthetic oils will include diester oils such as di(2-ethylhexyl) sebacate, azelate and adipate; complex ester oils such as those formed from dicarboxylic acids, glycols and either monobasic acids or monohydric alcohols; silicone oils; sulfide esters; organic carbonates; and other synthetic oils known to the art.

Other additives, of course, may be added to the oil compositions of the present invention to form a finished oil. Such additives may be the conventionally used additives including oxidation inhibitors such as phenothiazine or phenyl α-naphthylamine; rust inhibitors such as lecithin or sorbitan monoleate; detergents such as barium phenates; pour point depressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; viscosity index improvers such as olefin copolymers, polymethacrylates; etc. A particularly useful additive is the basic alkaline earth metal salts of an organic sulfonic acid, generally a petroleum sulfonic acid or a synthetically prepared alkaryl sulfonic acid. Among the petroleum sulfonates, the most useful products are those prepared by the sulfonation of suitable petroleum fractions with subsequent removal of acid sludge and purification. Synthetic alkaryl sulfonic acids are usually prepared from alkylated benzenes such as the Friedel-Crafts reaction product of benzene and a polymer such as tetrapropylene. Suitable acids may also be obtained by sulfonation of alkylated derivatives of such compounds as diphenylene oxide thianthrene, phenolthioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexane, decahydro naphthalene and the like.

Basic alkaline earth metal sulfonates are generally prepared by reacting an alkaline earth metal base, e.g. lime, magnesium oxide, magnesium alcoholate with CO_2 in the presence of sulfonic acid or neutral metal sulfonates, ordinarily the calcium, magnesium or barium salts. These neutral salts in turn may be prepared from the free acids by reaction with the suitable alkaline earth metal base, or by double decomposition of an alkali metal sulfonate, which methods are well known in the art. Further details are described in U.S. Patent No. 3,562,159.

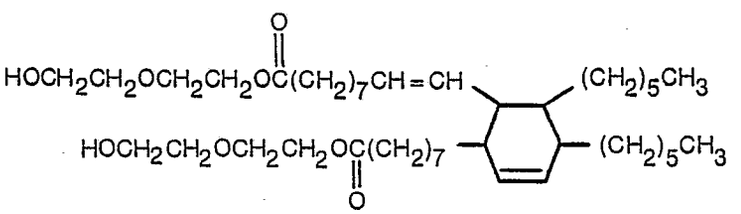
The composition of this invention is particularly useful when metal containing additives such as the normal and basic metal phenates, sulfonates or sulfurized phenates are used since such components have been known to cause compatibility problems in more conventional type lubricant compositions.

The above described additive package may be used in conventional base oils with other conventional additives. While the components can generally be added in their normal and conventional manner, it is a preferred embodiment of this invention to keep the zinc dihydrocarbyl dithiophosphate and polycarboxylic acid/glycol or glycerol ester components apart from one another until at least one of such components has been predispersed as described in U.S. 4,105,571. This will help to maintain a storage stable and compatible composition. By predispersed it is meant that the ester component or the zinc component or both separately are mixed with the ashless dispersant, which may be in oil solution, until the solution is generally clear.

The following examples are further illustrative of this invention and are not intended to be construed as limitations thereof.

Example 1

Formulations were prepared using a 10W—40SE quality automotive engine oil containing 1.5% by weight, based on the total lubricating oil weight, of zinc dialkyl dithiophosphate (80% active ingredient in diluent mineral oil) in which the alkyl groups were a mixture of such groups having between 4 and 5 carbon atoms and made by reacting P_2S_5 with a mixture of about 65% isobutyl alcohol and 35% of amyl alcohol; 0.1% by weight, based on the total lubricating oil weight of an ester formed by esterification of a dimer acid of linoleic acid and diethylene glycol and having the formula:



This additive is actually a mixture of the structure shown plus higher molecular weight repeating units (polymers) of this material.

Dispersants containing different amounts of free hydroxyl contents were used in the different lubricating formulations as described below:

A) 5.25% by wt. of dispersant (mixture of 46.5% by weight active ingredient in mineral lubricating oil) was used, said dispersant prepared by reacting polyisobutenyl succinic anhydride (PIBSA), the polyisobutenyl radical (PIB) having an average molecular weight ($\bar{M}n$) of about 900 with an equal molar amount of pentaerythritol and a minor amount of a polyamine mixture comprising polyoxypropylene amine and polyethylene amines to form a product having a nitrogen content of about 0.35% by weight and having a millimole (mM) hydroxyl per gram of active ingredient of 2.00. Materials of this type are described in U.S. Patent 3,804,763 and sold by Lubrizol Corporation under the tradename Lubrizol 6401;

B) A dispersant similar to A described above but having about 75% of the pentaerythritol added was prepared and had a nitrogen content of 0.27% and 1.55 mM of hydroxyl per gram of active ingredient;

C) Another dispersant similar to A described above but using about 50% of the pentaerythritol was prepared and had a nitrogen content of 0.44% and 1.25 mM of hydroxyl per gram of active ingredient;

D) Another dispersant similar to A described above was prepared using 10% of pentaerythritol and had a nitrogen content of 1.05% and 0.75 mM of hydroxyl per gram of active ingredient.

The dispersants noted above were added to the 10W—40SE crankcase oil along with the other additives and a rust inhibitor, i.e. overbased magnesium sulfonate, a detergent and a VI improver, i.e. an ethylene-propylene copolymer.

The above noted compositions all exhibited storage stability and compatibility over an extended period and were further tested for relative friction using a ball on cylinder test.

The apparatus used in the ball on cylinder test is described in the Journal of the American Society of Lubrication Engineers, entitled "ASLE Transactions", Vol. 4 pages 1—11, 1961. In essence, the apparatus consists basically of a fixed metal ball loaded against a rotating cylinder. The weight on the ball and the rotation of the cylinder can be varied during any given test or from test to test. Also, the time of any given test can be varied. Generally, however, steel on steel is used at a constant load, a constant rpm and a fixed time and in each of the tests of this example, a 4 Kg load, 0.26 rpm and 70 minutes was used. The actual friction was determined from the power actually required to effect rotation and the relative friction determined by ratioing the actual load to that of a standard. The apparatus and method used is more fully described in U.S. Patent No. 3,129,580 which was issued May 21, 1964 to Furey et al and which is entitled "Apparatus for Measuring Friction and Contacts Between Sliding Lubricating Surfaces".

The results of ball on cylinder test are given below:

Composition	mM OH per gram of Active Dispersant	Coeff of Frict. @70 Min.
A	2.0	.135
B	1.55	.095
C	1.25	.075
D	0.75	.055

While noting in the above composition that the amount of friction was significantly reduced by decreasing the hydroxyl content, it was ascertained that a level of about 0.35 mM OH/gram of active dispersant was needed to have a compatible system. Thus, the surprising friction effects of using the composition of this invention wherein a dispersant having selected hydroxyl content is used is readily shown by the results.

Claims

1. A lubricating oil composition comprising, per 100 parts by weight, a major proportion of lubricating oil, a total of from 0.01 to 2.0 parts by weight of one or more esters of a polycarboxylic acid with a glycol or glycerol, and a total of from 0.01 to 5.0 parts by weight of one or more zinc dihydrocarbyl dithiophosphates; further containing a total of 0.1 to 20 parts by weight of one or more hydroxyl containing ashless dispersants having a high molecular weight aliphatic oil solubilizing group attached thereto, characterized in that said dispersant(s) contain(s) from 0.35 to 1.8 millimoles of free hydroxyl groups per gram of active ingredient(s) in the dispersant(s).

2. A composition as claimed in claim 1, wherein said dispersant contains from 0.5 to 1.5 millimoles of free hydroxyl groups per gram of active ingredient(s) in the dispersant.

3. A composition as claimed in claim 1 or claim 2, wherein said dispersant is derived from an alkenyl succinic acid or anhydride, in which said alkenyl group has a molecular weight of at least 900.

4. A composition as claimed in claim 1 or 2, wherein said dispersant is nitrogen-containing alkenyl succinic acid or anhydride, or is an ester of an alkenyl succinic acid or anhydride with polyhydric alcohols, phenols or naphthols.

5. A composition as claimed in any preceding claim, wherein said polycarboxylic acid ester(s) component is formed from a dicarboxylic acid having from 9 to 42 carbon atoms between the carboxylic acid groups and a glycol selected from alkane diols having from 2 to 12 carbon atoms and oxa-alkane diols having from 4 to 200 carbon atoms.

6. A composition as claimed in claim 4, wherein said polycarboxylic acid ester(s) component is formed from a dimer acid of a conjugated fatty acid having from 16 to 22 carbon atoms between carboxylic acid groups.

7. A composition as claimed in claim 6, wherein said ester is formed by the esterification of a dimer acid of linoleic acid and diethylene glycol.

8. A composition as claimed in any preceding claim, wherein the dihydrocarbyl groups of said zinc compound are alkyl groups of from 2 to 8 carbon atoms.

9. A composition as claimed in any preceding claim, further containing a metal containing additive comprising a normal or basic metal phenate, sulfonate or sulfurized phenate.

10. A method of preparing the lubricating composition defined in any preceding claim, characterized by predispersing either said zinc dihydrocarbyl dithiophosphate or said ester of polycarboxylic acid, or both separately, in at least some of said dispersant prior to incorporation thereof into the lubricating oil composition.

11. A method of reducing friction in an internal combustion engine comprising lubricating the engine using the lubricating oil composition claimed in any one of claims 1 to 9.

Revendications

1. Composition d'huile lubrifiante comprenant, pour 100 parties en poids, une proportion majeure d'huile lubrifiante, un total de 0,01 à 2,0 parties en poids d'un ou plusieurs esters d'un polyacide carboxylique et d'un glycol ou de glycérol et un total de 0,1 à 5,0 parties en poids d'un ou plusieurs dihydrocarbyl dithiophosphates de zinc, contenant en outre un total de 0,1 à 20 parties en poids d'un ou plusieurs dispersants sans cendres contenant des groupes hydroxyles et sur lesquels est fixé un groupe aliphatique de poids moléculaire élevé solubilisant dans l'huile, caractérsé en ce que ce dispersant (ces dispersants) contient (contiennent) 0,35 à 1,8 millimoles de groupes hydroxyles libres par gramme d'ingrédient actif (d'ingrédients actifs) du dispersant.

2. Composition selon la revendication 1, caractérisée en ce que ce dispersant contient 0,5 à 1,5 millimoles de groupes hydroxyles libres par gramme d'ingrédient actif (d'ingrédients actifs) du dispersant.

3. Composition selon la revendication 1 ou 2, caractérisée en ce que ce dispersant est un dérivé d'un acide ou d'un anhydride alkényl succinique dans lequel le groupe alkényle a un poids moléculaire d'au moins 900.

4. Composition selon la revendication 1 ou 2, caractérisée en ce que ce dispersant est un acide ou un anhydride alkényl succinique contenant de l'azote ou est un ester d'un acide ou d'un anhydride alkényl succinique et de polyalcools, de polyphénols ou de polynaphtols.

5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que l'ester (les esters) de polyacide(s) carboxylique(s) est formé (sont formés) à partir d'un diacide carboxylique ayant 9 à 42 atomes de carbone entre les groupes acides carboxyliques et d'un glycol choisi parmi les alcane diols ayant 2 à 12 atomes de carbone et les oxa-alcane diols ayant 4 à 200 atomes de carbone.

6. Composition selon la revendication 4, caractérisée en ce que l'ester (les esters) de polyacide(s) carboxyliques est formé (sont formés) à partir d'un acide dimère d'un acide gras conjugé ayant 16 à 22 atomes de carbone entre les groupes acides carboxyliques.

7. Composition selon la revendication 6, caractérisée en ce que cet ester est formé par estérification d'un acide dimère de l'acide linoléique par le diéthylèneglycol.

8. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que les groupes dihydrocarbyles du dérivé du zinc sont des groupes alkyles de 2 à 8 atomes de carbone.

9. Composition selon l'une quelconque des revendications précédentes, contenant en outre un additif contenant un métal, comprenant un phénate, un sulfonate ou un phénate sulfuré de métal normal ou basique.

10. Procédé de préparation de la composition lubrifiante définie dans l'une quelconque des revendications précédentes, caractérisée en ce que l'on disperse préalablement le dihydrocarbyle dithiophosphate de zinc ou l'ester de polyacide carboxylique ou les deux séparément dans au moins une certaine quantité du dispersant avant de les incorporer à la composition d'huile lubrifiante.

11. Procédé pour diminuer le frottement dans un moteur à combustion interne comprenant la lubrification du moteur par emploi de la composition d'huile lubrifiante revendiquée dans l'une quelconque des revendications 1 à 9.

Patentansprüche

1. Schmierölzusammensetzung, die je 100 Gewichtsteile einen überwiegenden Anteil Schmieröl, insgesamt 0,01 bis 2,0 Gewichtsteile von einem oder mehreren Estern einer Polycarbonsäure mit einem Glykol oder Glycerin, insgesamt 0,01 bis 5,0 Gewichtsteile eines oder mehrere Zinkdihydrocarbyldithiophosphate und außerdem insgesamt 0,1 bis 20 Gewichtsteile von einem oder mehreren hydroxylhaltigen aschefreien Dispersionsmitteln mit einer daran gebundenen hochmolekularen aliphatischen öllöslichmachenden Gruppe enthält, dadurch gekennzeichnet, daß das Dispersonsmittel bzw. die Dispersionsmittel 0,35 bis 1,8 mMol freie Hydroxylgruppen je g aktive(r) Bestandteil(e) in dem (den) Dispersionsmittel(n) enthält bzw. enthalten.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Dispersionsmittel 0,5 bis 1,5 mMol freie Hydroxylgruppen je g aktive(r) Bestandteil(e) im Dispersionsmittel enthält.

3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß sich das Dispersionsmittel von einer Alkenylbernsteinsäure oder einem Alkenylbernsteinsäureanhydrid ableitet, wobei die Alkenylgruppe ein Molekulargewicht von mindestens 900 besitzt.

4. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Dispersionsmittel stickstoffhaltige Alkenylbernsteinsäure oder stickstoffhaltiges Alkenylbernsteinsäureanhydrid oder ein Ester einer Alkenylbernsteinsäure oder von Alkenylbernsteinsäureanhydrid mit mehrwertigen Alkoholen, Phenolen oder Naphtolen ist.

5. Zusammensetzung nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die Polycarbonsäureesterkomponente aus einer Dicarbonsäure mit 9 bis 42 Kohlenstoffatomen zwischen den Carbonsäuregruppen und einem Glykol ausgewählt aus Alkandiolen mit 2 bis 12 Kohlenstoffatomen und Oxa-Alkandiolen mit 4 bis 200 Kohlenstoffatomen hergestellt ist.

6. Zusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß die Polycarbonsäureesterkomponente aus einer dimeren Säure einer konjugierten Fettsäure mit 16 bis 22 Kohlenstoffatomen zwischen den Carbonsäurengruppen hergestellt ist.

7. Zusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß der Ester durch Veresterung einer dimeren Säure von Linolsäure und Diethylenglykol hergestellt ist.

8. Zusammensetzung nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die Dihydrocarbylgruppen der Zinkverbindung Alkylgruppen mit 2 bis 8 Kohlenstoffatomen sind.

9. Zusammensetzung nach einem der vorangehenden Ansprüche dadurch gekennzeichnet, daß sie ein metallhaltiges Additiv enthält, das ein normales oder basisches Metallphenat, -sulfonat oder sulforiertes -phenat umfaßt.

10. Verfahren zur Herstellung der Schmiermittelzusammensetzung gemäß der vorangehenden Ansprüche, dadurch gekennzeichnet, daß entweder das Zinkdihydrocarbyldithiophosphat oder der Ester der Polycarbonsäure oder beide getrennt in mindestens einem Teil des Dispersonsmittels vor der Einverleibung in die Schmierölzusammensetzung vordispergiert wird bzw. werden.

11. Verfahren zur Verringerung der Reibung bei einem Verbrennungsmotor, dadurch gekennzeichnet, daß der Motor unter Verwendung der Schmierölzusammensetzung gemäß einem der Ansprüche 1 bis 9 geschmiert wird.