The load-bearing capability of certain cyclic carbon-containing compounds particularly suited for use as a fluid component of tractive drives is substantially improved without impairing the oxidative stability or coefficient of traction of the fluid by incorporating minor amounts of zinc di(neo-alkyl)phosphorodithioate.
LUBRICANTS HAVING IMPROVED LOAD-BEARING PROPERTIES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 26,446, filed Apr. 7, 1970, and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to functional fluid compositions particularly adapted for use as lubricants in tractive drives, and more specifically, to additives for increasing the load-carrying capability of these compositions.

2. Description of Prior Art

A tractive drive is a device in which torque is transmitted from an input element to an output element through nominal point or line contact, typically with a rolling action, by virtue of the traction between the contacting elements. While tractive elements are commonly spoken of as being in contact, it is generally accepted that a fluid film is provided therebetween. Almost all tractive drives require fluids to remove heat, to prevent wear at the contact surfaces, and to lubricate the contacting elements, internal bearings and other moving parts associated with the drive. The lubricating fluid between the contacting elements is subjected to extremely high stress and it is essential that the composition have a high load-carrying capability in order to assure long life for the contacting elements.

Fluid compositions used in tractive drives are also useful as general lubricants for roller and ball bearings and other mechanical devices having elements in rolling contact. Like tractive devices, the load-carrying capability of the lubricant is an important consideration for many high stress applications. One particularly important application is found in lubricating jet engine bearings where such compositions are effective to reduce bearing wear by reducing the propensity of the bearings to skid.

It is accordingly an object of the present invention to provide lubricating compositions having improved load-carrying capability and antiwear characteristics. It is another object of this invention to provide a class of additives to improve the load-carrying capability of certain compositions useful as tractive fluids without adversely affecting the tractive coefficient or the high temperature oxidation stability of the fluid. These and other objects of this invention will be apparent from the ensuing description of the invention.

SUMMARY

The load-carrying capability of certain lubricating base stocks comprising compounds having from 10 to about 70 carbon atoms and including at least two cyclohexyl groups is improved by incorporating into the base stock a minor amount of zinc di(alkyl)phosphorodithioate wherein the alkyl groups have from 5 to about 13 carbon atoms and may be the same or different. The addition of this material to the lubricant base stock composition significantly increases the load-carrying capability of the composition as measured by standard wear tests without significantly diminishing the high temperature oxidation stability as indicated by change in viscosity and corrosivity. Preferred additives are zinc di(neo-hexyl)phosphorodithioate, zinc di(neo-pentyl)phosphorodithioate and mixtures thereof.

DESCRIPTION OF PREFERRED EMBODIMENTS

The compositions of the present invention which are generally useful as lubricants and particularly useful as lubricants for tractive devices are comprised of a major amount of a base stock as hereinafter defined and a minor amount of a zinc di(alkyl)phosphorodithioate inhibitor.

The base stocks of the instant invention are comprised of a major amount of one or more cyclohexyl compounds having two or more cyclohexyl rings which are fused, concatenated, or linked by a C1 to C14 alkylene, a carboxy, or an ether linkage, and having a total of from 10 to about 70 carbon atoms. Preferred compounds are those having from 2 to about 6 cyclohexyl rings, and more preferably from 2 to 4 such rings. A compound having 3 or more cyclohexyl rings may have a structure which includes combinations of fused and/or concatenated and/or linked cyclohexyl rings.

The cyclohexyl compounds are known to have good lubricating properties and relatively high coefficients of traction as disclosed in U.S. Pat. No. 3,440,894. In addition to such cyclohexyl compounds, the base stocks of the present lubricating compositions may contain minor amounts of other lubricating compositions including, for example, paraffinic and naphthenic petroleum oils, C6-C8 polyolefins and synthetic lubricants such as mono- and dicarboxylic acid esters. The utility and operability of the instant invention is in no way negated by the inclusion of minor amounts of such non-critical base stock constituents in combination with the cyclohexyl compound which is the essential component.

As used herein the term "major amount" is defined to mean amounts greater than 50 percent by weight and the term "minor amount" means amounts less than 50 percent by weight. While the compositions of this invention must contain at least a major amount of a cyclohexyl compound as hereinafter defined, it is generally preferred that the cyclohexyl compound be present in amounts of about 65 percent by weight and more preferably at least about 85 percent by weight of the total composition.

Examples of representative concatenated and linked cyclohexyl compounds include dicyclohexyl, 4-(1-methylthylidicyclohexyl, 4,4'-bis(1-methylthylidicyclohexyl, x-isohexyl-x'-isopropylidicyclohexyl, x-cyclopentylidicyclohexyl, dicyclohexylmethane, (x-ethylcyclohexyl)cyclohexylmethane, [x-cyclohexyl(1-methylthyl)]cyclohexylmethane, bis(2,4,6-trimethylcyclohexyl)methane, 1,1-dicyclohexylethane, 1,1,3-tricyclohexylpropane, 1,2,3-tricyclohexylpropane, trimethylolpropane tricyclohexanecarboxylate, 1,2-tercyclohexyl-m-tercyclohexyl, x-(1,1-dimethylbutyl)-1,3-tercyclohexyl, x-(1,1-dimethylbutyl)-1,2-tercyclohexyl, 1,2-isopropyltercyclohexyl, 1,3-isopropyltercyclohexyl, bis(1,3-cyclohexyloxy)cyclohexane, 1,2-bis(methylocyclohexyl)cyclohexane, dicyclohexyl cyclohexane-1,3-dicarboxylate, x'-quatercyclohexyl, tricyclohexylmethane, bis-, cis- and trans-1,2-cyclohexyl cyclohexanedicarboxylate, 1,1-dicyclohexyl-2-methylpropane, 1,1-dicyclohexyl-2-methylbutane, 1,1-dicyclohexyl-2,5-dimethylhexane, 1,1-dicyclohexylpentane, 1,2-dicyclohexylpropane, 1,2-di(x-ethylcyclohexyl)-
propane, 2,2-dicyclohexylpropane, 2,3-dicyclohexyl-2,3-dimethylbutane, 1,3-dicyclohexyl-2-methylbutane, 1,3-dicyclohexylbutane, and 2,4-dicyclohexyl-2-methylpentane. A particularly preferred class of such compounds are those selected from the group consisting of dicyclohexyl, allyl dicyclohexyl, tercyclohexyl, alkyl tercyclohexyl, quatercyclohexyl, quinuicyclo-

hexyl, 2,3-dicyclohexyl-2,3-dimethylbutane, and mixtures thereof, wherein the alkyl contains from 1 to about 18 carbon atoms.

Examples of fused ring cyclohexyl compounds and compounds having structures including combinations of fused, concatenated, and/or linked cyclohexyl groups include cisdecalin, trans-decalin, 2,3-dimethyldecalain, isopropyldecalin, t-butyldecalin, perhydrofluorone, perhydrophenanthrene, perhydrodicyclopentadiene (trimer), perhydrocyclopenta diene trimer, perhydrofluoranthene, the cyclohexyl-1,3,3-trimethylindane, x-hexylperhydro fluoranthenes, x-cyclohexylperhydrofluoranthenes, poly(ethyl-1-methyl)-perhydrofluoran thanes, x-isopropylperhydrofluoranthenes, perhydrofluorenex-cyclohexyl, perhydrofluorenex-isoodecyl, 1-cyclohexyldecan, 2-(cyclohexyl-x-methyl) bicyclo[2,2,1]heptane, perhydropyrene, ethylperhydrofluorene, perhydroanthracene, bis-2-decalin, 1-cyclohexyldecan, 2-cyclohexyldecan, dimethyl cy clohexyldecan, 4,5-methyleneperhydrophenanthrene, 1,3-dicyclohexyloxycyclohexane, and cyclohexyl decalylcyclohexyl dilinether. A particularly preferred class of such compounds are those selected from the group consisting of decalin, cyclohexyldecalin, alkyl substituted decalin, alkyl substituted cyclohexylde calin, and mixtures thereof, wherein the alkyl contains from 1 to about 18 carbon atoms.

In addition to the base stock materials and the zinc di(neo-alkyl)phosphorodithioate inhibitor, the compositions of this invention may contain other additive materials including for example viscosity index improvers, antioxidants, antiwear agents, corrosion inhibitors, dispersants, dyes, antifoam agents and the like.

Viscosity index improvers useful in the lubricating compositions of the present invention may be any of the polymeric materials commonly employed in the art. Particularly preferred are the polymers of alkyl esters of α,β-unsaturated monocarboxylic acids, including for example, poly(4-butylmethacrylate), poly(4-hexylmethacrylate), poly(octylacrylates), and poly(dodecylacrylates). Also useful are polymers such as polyisobutylenex, alkylated polystrene, polyvinyl ethers, and copolymers of alkyl esters of monocarboxylic acids and other monomers copolymerizable therewith as for example, the copolymer of an alkyl methacrylate and vinyl pyridine. In a preferred embodiment of the present invention, the load-carrying and antiwear properties of the lubricating fluid are improved by incorporating into the fluid one or more zinc di-neo-alkylphosphorodithioate compounds wherein the neo-alkyl groups contain from 5 to about 13 carbon atoms and may be the same or different, as for example zinc di(neo-pentyl)phosphorodithioate, zinc di(neo-hexyl)phosphorodithioate, or zinc (neo-pentyl)(neo-hexyl)phosphorodithioate. Although zinc dialkyl phosphorodithioates generally are known to be antiwear agents, these compounds as a class have been found to be unsuitable for use in the base stocks of this invention because of an adverse ef

fect on oxidation resistance of the fluid. Examples of such known zinc dialkylphosphorodithioate antiwear agents which were evaluated and found to be unsuitable include the present antiwears. Examples of such known alkyl groups di(1,3-dimethylbutyl), 2-ethylhexyl-isopropyl, 2,3-ethylhexylisobutyl, isobutyl-2-ethylhexyl and di(n-hexyl).

In view of the consistently negative results obtained with many of the zinc dialkylphosphorodithioates on oxidation resistance of base stock material, it was most surprising and unexpected to find that one class of compounds, the zinc di(neo-alkyl)phosphorodithioates of this invention, and particularly zinc di(neo-alkyl)phosphorodithioate, significantly improved the load-carrying capability of the fluid without decreasing the oxidation resistance. The effectiveness of the additive was especially surprising since many of the unsatisfactory compounds were recognized antitrust agents generally useful in functional fluids. The n-alkyl equivalent of the preferred additive of this invention, zinc di(n-hexyl)phosphorodithioate, for example, reduced the oxidation resistance of the base stock as evidenced by a large increase in viscosity during a standard oxidation test. Likewise the 1,2-dimethylbutyl compound caused a major increase in viscosity of the fluid in the oxidation test, and the isobutyl 2-ethylhexyl and 2-ethylhexyl isopropyl compounds each caused substantial increases in corrosivity of the fluid. On the basis of the unfavorable results obtained with these compositions, the excellent results obtained with the di(neo-alkyl)additives of this invention were not to be predicted.

In accordance with the present invention, zinc di(neoalkyl)phosphorodithioate is added to the base stock at a concentration of at least about 0.1 percent by weight of the base stock, and preferably at a concentration of from about 0.5 to about 2 percent by weight. Higher concentrations can of course be used, but no substantial improvement in results is generally obtained thereby.

The nature and advantages to be gained by means of the present invention are illustrated in the examples which follow. These examples are presented for purposes of illustration only, and the invention is not intended to be limited to the specific embodiments presented therein.

In the following examples, the coefficients of friction was determined on the "Thrust Bearing Test Machine" described in "Effect of Lubricant Composition on Friction as Measured With Thrust Ball Bearings" by F. G. Rounds [J. Chem. Eng. Data, Vol. 5, No. 4, pp. 499 (1960)]. This machine measures the torque transmitted from a central drive shaft to a torque arm through two thrust ball bearings which are submerged in the test fluid. The bearings are shaft-mounted and can be rotated while being subjected to an axial thrust load. Thrust loads are applied hydraulically or by compressing calibrated Belleville springs. A tachometer geared to the drive shaft measures the rotational speed. Thermocouples located within ¼-inch of the balls of the test bearings measure the test fluid temperature which is held constant at various predetermined temperatures by heating or cooling the jacket fluid in the housing surrounding the test chamber.

The individual balls tend to spin on an axis parallel to the principal bearing axis as well as roll around the raceway. As a result, both rolling and sliding actions contribute to the friction. The output torque is measured with the torque arm which is fitted between the two bearings. This measured torque is then interpreted.
The Wear Scar Test Data was obtained according to the standard Shell 4-ball test, operated with 52100 steel balls at 200° F. and 1260 rpm. under a 40 kgm. load.

The data in Table I below illustrates the advantages of zinc di(neo-alkyl) phosphorodithioates over related compounds in a typical tractant composition consisting of a mixture of dicyclohexyl, terecyclohexyl and 2,3-dicyclohexyl-2,3-dimethylbutane containing 1.5 percent of an alkyl methacrylatevinyl pyrrolidone copolymer as a V. I. improver.

<table>
<thead>
<tr>
<th>Example</th>
<th>Additive(1)</th>
<th>Coefficient of Traction</th>
<th>Viscosity(2)</th>
<th>O &amp; C Test Copper Corrosion(3)</th>
<th>Wear Scar Test (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None (Control)</td>
<td>0.0618</td>
<td>6</td>
<td>-0.04</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>1% di(neo-hexyl)</td>
<td>0.0638</td>
<td>13</td>
<td>-0.40</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>1% di(neo-pentyl)</td>
<td>5</td>
<td>-1.3</td>
<td>-</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>1% di(neo-hexyl)</td>
<td>0.0629</td>
<td>2050</td>
<td>-1.03</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1% 1,3-dimethylbutyl</td>
<td>180</td>
<td>-0.7</td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>1% 2-ethylhexyl isopropyl</td>
<td>2344</td>
<td>-3.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1% isobutyl-2-ethylhexyl</td>
<td>1800</td>
<td>-7.7</td>
<td>-</td>
<td>0.49</td>
</tr>
<tr>
<td>8</td>
<td>2% 2-ethylhexyl isopropyl</td>
<td>0.0623</td>
<td>24</td>
<td>-5.4</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) Zinc (alkyl alkyl) phosphorodithioate, % by weight of base fluid
(2) Viscosity increase at 100°F. — Specification: less than 30
(3) Mg. metal loss; cm. surface area — Specification: less than -0.6
(4) Scar diameter — Specification: less than 0.45 mm.

It is apparent from the above data that substantial improvement in the load-carrying capability of the fluid is obtained by the addition of as little as 0.1 percent of zinc di(neo-hexyl) phosphorodithioate. Although the preceding description and examples have been directed primarily toward the use of zinc di(neo-pentyl)- and di(neo-hexyl) phosphorodithioate as the additives of this invention, the neo-alkyl grounds may be different and may contain up to about 13 carbon atoms. Included, therefore, within the scope of the present invention are, for example, zinc di(neo-alkyl) phosphorodithioates wherein the neo-alkyl group is neo-heptyl, neo-ocytol, neo-decyl, neo-undecyl, neo-dodecyl, neo-tridecyl, and mixtures thereof.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A lubricating composition consisting essentially of A. a base stock selected from the group consisting of dicyclohexyl, alkyl dicyclohexyl, terecyclohexyl, alkyl terecyclohexyl, quatercyclohexyl, quinquecyclohexyl, 2,3-dicyclohexyl-2,3-dimethylbutane and mixtures thereof, wherein the alkyl contains from 1 to about 18 carbon atoms, and
2. An amount of at least about 0.1 percent by weight of the base stock and sufficient to improve the load-carrying capability of the base stock of a zinc di(neo-alkyl) phosphorodithioate wherein the neo-
alkyl groups contain from about 5 to 13 carbon atoms and may be the same or different.

2. A lubricating composition consisting essentially of
   A. a base stock selected from the group consisting of decalin, cyclohexyldecalin, alkyl substituted decalin, alkyl substituted cyclohexyldecalin, and mixtures thereof, wherein the alkyl contains from 1 to about 18 carbon atoms, and
   B. an amount of at least about 0.1 percent by weight of the base stock and sufficient to improve the load-carrying capability of the base stock of a zinc di(neo-alkyl) phosphorodithioate wherein the neo-alkyl groups contain from about 5 to 13 carbon atoms and may be the same or different.

3. A composition of claim 1 wherein the zinc di(neo-alkyl) phosphorodithioate is selected from the group consisting of zinc di(neo-pentyl)phosphorodithioate, zinc di(neo-hexyl)phosphorodithioate and mixtures thereof.

4. A composition of claim 1 wherein the amount of the zinc di(neo-alkyl)phosphorodithioate is from about 0.5 to 2 percent by weight of the base stock.

5. A composition of claim 1 wherein the base stock comprises a mixture of dicyclohexyl, tercyclohexyl and 2,3-dicyclohexyl-2,3-dimethylbutane.

6. A composition of claim 5 wherein the zinc di-(neo-alkyl)phosphorodithioate is zinc di(neo-hexyl)phosphorodithioate.

7. A composition of claim 2 wherein the zinc di-(neo-alkyl)phosphorodithioate is selected from the group consisting of zinc di(neo-pentyl)phosphorodithioate, zinc di(neo-hexyl)phosphorodithioate and mixtures thereof.

8. A composition of claim 2 wherein the amount of zinc di(neo-alkyl)phosphorodithioate is from about 0.5 to 2 percent by weight of the base stock.