

## Description

This invention relates to the use of oil-soluble or oil-dispersible metallic compounds for retarding soot related viscosity rate increases in lubricants for diesel engines.

Lubricants, particularly lubricants for diesel engines used in low speed, high torque operations, suffer from a viscosity build-up over time. This viscosity build-up is manifested in that the lubricant within the diesel engine begins a gradual viscosity rise and that the rate of viscosity increase accelerates with time. Eventually, the viscosity increase becomes sufficiently high and the oil flow within the engine will be restricted.

A second factor is that the lubricant in the sump gradually thickens and becomes unavailable for lubrication. When the thickened lubricant does not pass the oil pump inlet, engine damage results.

The viscosity build-up thus can lead to unacceptable wear in the engine, particularly in a cold climate. The main preventative technique for avoiding damage from excessive viscosity build-up is to drain a small amount of oil from the sump and to observe the viscosity of the lubricant. The problem then becomes the determination of the correct interval for checking the sump. As the rate of change in viscosity accelerates, the intervals for checking lubricant viscosity must become more closely spaced to ensure that engine damage does not occur.

It has been stated in a paper entitled, Oil Thickening In the Mack T-7 Engine Test by Covitch, Humphrey and Ripple, that various compounds may be added to a diesel lubricant to limit oil thickening. The Covitch et al paper was presented at the SAE Fuels and lubricants meeting, Tulsa, Oklahoma on October 23, 1985. The Covitch et al paper teaches that soot, which is produced as an incomplete combustion product in diesel engines, finds its way into the lubricating oil. The presence of soot in the crankcase has been linked to viscosity increase and viscosity rate increase in the lubricants.

It has been suggested in the application of Koch et al US-A-4816038 EP-A-238632 that various metal complexes of Mannich bases of transition metals may be utilized in fuels. Koch et al also suggest that a Schiff base may be incorporated into their compositions. Dorer et al US-A-4664677 EP-A-0159333 suggests that mixtures of manganese containing salts and hydrocarbon-soluble copper containing salts may be utilized as fuel additives to reduce the ignition temperature of exhaust particulates from diesel engines.

Diesel lubricants containing alkali metal salts as additives to minimize undesirable viscosity increases in diesel engines are described in AU-P-591710. The Ripple application further describes dispersants which are useful in diesel crankcase lubricants. Transition metal containing hydrocarbon soluble compositions containing ashless dispersants and phenolic anti-oxidants are disclosed in AU-A-578726.

United States Reissue Patent 29,661 which was granted on June 6, 1978 to Hendrickson describes a test composition comprising SAE neutral refined oil containing a succinimide dispersant, calcium phenates and as an oxidation catalyst, a solution of metal naphthenates in kerosene including copper, iron, tin, manganese and lead. The purpose of including the metals in the Hendrickson patent is apparently to rapidly increase the oxidation of the oil as a part of a test of the effectiveness of the dispersant employed.

United States Patent 4,529,408 issued July 16, 1985 to Yan suggests that coal combustion may be improved, ash corrosion modified, and fouling and ash slagging reduced by including a metal at a few parts per thousand with coal. The materials suggested by Yan include a member selected from the group consisting of manganese dioxide, iron oxide, manganese nodules, sand and mixtures thereof.

Johnson, in United States Patent 4,411,774 issued October 25, 1983 suggests that waste oil contains in parts per million concentration various metals including tin, lead, copper, aluminum, iron, chromium, zinc, magnesium, nickel, barium, sodium, calcium, vanadium, molybdenum, boron and manganese. The waste oil, according to Johnson, also may contain silicon, phosphorus and possibly silver.

Hotten, in United States Patent 4,049,562, issued September 20, 1977 suggests that the anti-oxidant activity of an oil may be tested in the presence of a solution containing the naphthenates of copper, iron, manganese, lead and chromium. It is further stated by Hotten that this distribution of metals would be expected to be found in a used crankcase oil from a diesel engine.

Various transition metals as oxidation inhibitors are described in United States Patent 4,122,033 issued October 24, 1978 to Black. Watson, in United States Patent 3,652,616 issued March 28, 1972 describes fuel and lubricant compositions containing metals such as zinc, manganese, chromium, copper, cobalt, vanadium, titanium, molybdenum, silver, cadmium, tungsten or mercury. The use of copper as an anti-oxidant in lubricants is disclosed in European application 0024 146 to Colelough published February 25, 1981.

It has been found in the present invention that relatively small amounts of certain transition metals may be utilized in an oil-soluble form in a diesel lubricant composition to substantially reduce the soot related viscosity increase and the viscosity rate increase (acceleration). The compositions used in the present invention are particularly effective in diesel oils which are subject to rapid viscosity build-up.

Throughout the specification and claims, percentages and ratios are by weight, temperatures are in degrees Celsius unless otherwise indicated.

According to the present invention there is provided use of an oil-soluble or oil-dispersible metallic compound wherein the metal is selected from manganese, titanium, cobalt and mixtures thereof, for  
 5 retarding soot related viscosity rate increase of a lubricant in a diesel engine lubricating system prone to soot build-up, wherein the metallic compound is present as a metal at 30 ppm to 500 ppm of the lubricant.

Various preferred features and embodiments of the invention will now be described by way of non-limiting example.

This invention makes use of a composition comprising a polyvalent metal compound and a diesel  
 10 lubricating oil. The metallic compound includes both organic and inorganic forms of manganese, titanium, cobalt and mixtures thereof.

Preferably, the metallic compound contains manganese or titanium. Also useful herein are the metallic phenates, salicylates, phosphonates, dithiocarbamates and naphthenates. The naphthenates are a preferred species of the metallic compound.

15 Inorganic compounds include, for example, oxides, hydroxides, and carbonates. Organic and inorganic metal compounds are useful in mixtures within the present invention. The amount of metal employed should be sufficient to retard the viscosity rate increase between 100 and 150 hours in the Mack T-7 test. The viscosity rate increase slope should then be less than 0.1, preferably less than 0.08 during the 100 to 150 hour interval.

20 Preferred organic compounds useful for the metallic components are conveniently salts of at least one organic acid. While mixtures of organic and inorganic metal components are useful, it is highly desired that an organic metallic compound be employed to assist in dispersing the metal compound in the lubricant.

Organic acids used to make the salts for the metallic compound include carboxylic acids, particularly those containing from 1 to 30 carbon atoms, e.g., the carboxylates, sulfonic acids, particularly those  
 25 containing an aromatic ring structure (e.g., benzene ring) substituted with one or more alkyl groups of 4 to about 30 carbon atoms, e.g., a sulfonate, and phosphorus acids, containing within their structures one or more organic groups of 1 to about 30 or more carbon atoms. Preferably, the organic acid is a mixture of organic acids containing an average of at least 7 carbon atoms, conveniently about 4 to about 30, preferably 6 to 30 total carbon atoms per carboxyl group.

30 Such carboxylic, sulfonic and phosphorus acids are well known to the art. The carboxylic acids can be mono- or polycarboxylic acids (if the latter, typically they are di- or tricarboxylic acids).

Monocarboxylic acids include  $C_{1-7}$  lower acids (acetic, propionic, etc.) and higher  $C_8+$  acids (e.g., octanoic, decanoic, etc.) as well as the fatty acids of about 12-30 carbon atoms. The neo acids such as neo-octanoic and neodecanoic and the like are also useful.

35 The fatty acids are often mixtures of straight and branched chain acids containing, for example, from 5% to about 30% straight chain acids and about 70% to about 95% (mole) branched chain acids. Other commercially available fatty acid mixtures containing much higher proportions of straight chain acids are also useful. Mixtures produced from dimerization of unsaturated fatty acids can also be used.

40 Higher carboxylic acids include the well known dicarboxylic acids made by alkylating maleic anhydride or its derivatives. The products of such reactions are hydrocarbon substituted succinic acids, anhydrides, and the like. Lower molecular weight dicarboxylic acids, such as polymethylene bridged acids (glutaric, adipic, and the like), can also be used to make the salts of this invention as well as the lower molecular weight substituted succinic acids such as tetrapropenyl succinic acid and its analogs of to about  $C_{30}$  substituted acids.

45 Higher molecular weight substituted succinic anhydrides, acids, and analogs useful in making the salts of this invention have been described in a number of patents, particularly those dealing with acylated compounds useful as dispersants. Typical high molecular weight acids are those made by reacting a poly-(isobutene) fraction having between 30 and 400 (usually 50-250) carbon atoms with maleic anhydride. Such materials are described in U.S. Patents 3,172,892 issued to Le Suer et al on March 9, 1965, 3,219,866  
 50 issued to Norman et al on November 23, 1965, and 3,272,746 issued to Le Suer et al on September 13, 1966. Other monocarboxylic acids of similar molecular weight can be made by alkylating acrylic acid and its analogs. Mixtures of such acids can also be used.

The useful metallic compounds of this invention can also be made from carboxylic acids and even acidic hydroxy compounds such as alkylated phenols. Such materials are disclosed in U.S. Patent  
 55 4,100,082 issued to Clason et al on July 11, 1978, particularly columns 15-17.

Typically the organic acids used to make the salts of this invention are carboxylic acids, sulfonic acids, or mixtures thereof, or compounds containing both functional groups.

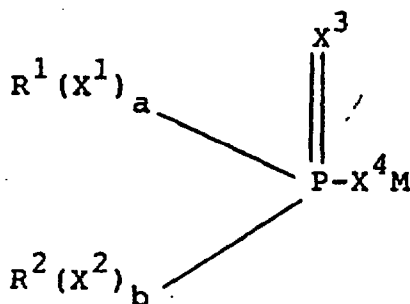
The sulfonic acids used to form the metallic compound include the aliphatic sulfonic acids. Examples of such sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fraction having a Saybolt Viscosity from about 100 seconds at 37°C to about 200 seconds at 99°C; petrolatum sulfonic acids; mono- and polywax substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, diphenyl amine, thiophene, alpha-chloronaphthalene, etc., other substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbons), cetylphenyl mono-sulfide sulfonic acids, dicetyl thianthrene disulfonic acids, dilauryl beta-naphthyl sulfonic acids, dicapryl nitronaphthalene sulfonic acids and alkaryl sulfonic acids such as dodecylbenzene (bottoms) sulfonic acids. Dodecylbenzene (bottoms) are principally mixtures of mono- and di-dodecylbenzenes.

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

Further details concerning sulfonic acids used herein can be found in U.S. Patents

| PATENT    | INVENTOR       | ISSUE DATE       |
|-----------|----------------|------------------|
| 2,616,905 | Asseff et al   | November 4, 1952 |
| 3,027,325 | McMillen et al | March 27, 1962   |
| 3,312,618 | Le Suer et al  | April 4, 1967    |
| 3,350,308 | McMillen et al | October 31, 1967 |
| 3,471,403 | Le Suer et al  | October 7, 1969  |
| 3,488,284 | Le Suer et al  | January 6, 1970  |
| 3,595,790 | Norman et al   | July 27, 1971    |
| 3,798,012 | Le Suer        | March 19, 1974   |
| 3,829,381 | Le Suer        | August 13, 1974  |
| 4,100,083 | Ripple         | August 22, 1978  |
| 4,326,972 | Chamberlin     | April 27, 1982   |

The useful salts of this invention can be made from phosphorus acids. Such phosphorus acids have been disclosed in a number of U.S. patents and other literature. Exemplary of the former is U.S. Patent 4,191,658 to Jahnke issued March 4, 1980, which discloses phosphorus acid salts of the formula



wherein M is the aforementioned metal of the metallic compound or mixtures thereof; each R<sup>1</sup> and R<sup>2</sup> is a hydrocarbon radical; each of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> and X<sup>4</sup> is oxygen or sulfur; and each of a and b is 0 or 1.

The salts made from organic acids can be prepared by reacting the organic acid with the metal, preferably manganese, for example, as manganese oxide, manganese hydroxide, and manganese carbonate.

A particularly preferred method of obtaining the metallic compound are as overbased salts. Overbased salts are those salts of organic acids which contain more than sufficient metal to neutralize the acid present. In other words, they contain in excess of one equivalent of metal per equivalent of acid derived moiety. Such salts are known to the art. For disclosures on overbasing in general, see, for example, U.S. Patent

3,827,979 to Piotrowski et al; U.S. Patent 3,312,618 to Le Suer et al issued April 4, 1967; U.S. Patent 2,616,904 and 2,616,905 to Asseff issued November 4, 1952; U.S. Patent 2,595,790 to Norman et al; and U.S. Patent 3,725,441 to Murphy et al issued April 3, 1973. For specific disclosures of overbased manganese and copper salts of organic acids, see U.S. Patents 2,695,910 issued November 30, 1954, to Asseff et al and 4,162,986 issued July 31, 1979, to Alkaltis et al.

In particularly preferred embodiments, this invention uses manganese salts of organic acids which are hydrocarbon-soluble. Highly overbased manganese metal organic compositions comprising a manganese oxide-hydroxide-carboxylate complex wherein the metal content is in chemical combination partly with oxygen in a polynuclear metal oxide crystallite core and partly with at least two different monocarboxylic acids or a mixture of one or more monocarboxylic and monosulfonic acids containing at least two carbon atoms as hydroxyl-metal-carboxylate and hydroxyl-metal sulfonate groups. See, for example, U.S. Patent 4,191,658 issued March 4, 1980, to Jahnke.

The metal compounds used in accordance with the invention are hydrocarbon soluble. As used herein, the term "hydrocarbon soluble" is intended to mean that the compounds are soluble or stably dispersible in normally liquid hydrocarbons. The term "stably dispersible" as used herein is intended to mean that the composition is capable of being dispersed in the lubricant to an extent which allows it to function in its intended manner. Thus, for example, a composition is hydrocarbon soluble if it is capable of being suspended in a lubricating oil in a manner sufficient to allow the oil to function as a lubricant.

The combination of the oil, the metallic compound and optionally the dispersant can be effected in any convenient manner. Mixtures of manganese and titanium, manganese and cobalt, and titanium and cobalt are also useful herein. Suggested metal molar ratios of the foregoing binary combinations are about 15:1 to 1:15, preferably about 10:1 to 1:10 of the first metal to the second metal.

The invention also contemplates the use of other additives. Such additives include, for example, detergents and dispersants of the ash-producing or ashless type.

The ash-producing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, 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 about 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 compound 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, carbital, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol, and amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-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 an elevated temperature 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 lubricant compositions of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 30 and preferably at least about 50 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:

|    | PATENT    | INVENTOR      | ISSUE DATE         |
|----|-----------|---------------|--------------------|
| 5  | 3,163,603 | Le Suer       | December 29, 1964  |
|    | 3,184,474 |               |                    |
|    | 3,215,707 | Rense         | November 2, 1965   |
| 10 | 3,219,666 | Norman et al  | November 23, 1965  |
|    | 3,271,310 | Le Suer       | September 6, 1966  |
|    | 3,272,746 | Le Suer et al | September 13, 1966 |
|    | 3,281,357 | Vogel         | October 25, 1966   |
| 15 | 3,306,908 | Le Suer       | February 28, 1967  |
|    | 3,311,558 | Prizer et al  | March 28, 1967     |
|    | 3,316,177 | Dorer         | April 25, 1967     |
| 20 | 3,340,281 | Brannen       | September 5, 1967  |
|    | 3,341,542 | Le Suer et al | September 12, 1967 |
|    | 3,346,493 | Le Suer       | October 10, 1967   |

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|    | 3,351,552 | Le Suer        | November 7, 1967   |
|    | 3,381,022 | Le Suer        | April 30, 1968     |
| 5  | 3,399,141 | Clemens        | August 27, 1968    |
|    | 3,415,750 | Anzenberger    | December 10, 1968  |
|    | 3,433,744 | Le Suer        | March 18, 1969     |
| 10 | 3,444,170 | Norman et al   | May 13, 1969       |
|    | 3,448,048 | Le Suer        | June 3, 1969       |
|    | 3,448,049 | Preuss et al   | June 3, 1969       |
|    | 3,451,933 | Leister        | June 24, 1969      |
| 15 | 3,454,607 | Le Suer        | July 8, 1969       |
|    | 3,467,668 | Gruber et al   | September 16, 1969 |
|    | 3,501,405 | Willette       | March 17, 1970     |
| 20 | 3,522,179 | Le Suer        | July 28, 1970      |
|    | 3,541,012 | Stuebe         | November 17, 1970  |
|    | 3,542,680 | Le Suer        | November 24, 1970  |
| 25 | 3,543,678 |                |                    |
|    | 3,567,637 | Sabol          | March 2, 1971      |
|    | 3,574,101 | Murphy         | April 6, 1971      |
| 30 | 3,576,743 | Widmer et al   | April 27, 1971     |
|    | 3,630,904 | Musser et al   | December 28, 1971  |
|    | 3,632,510 | Le Suer        | January 4, 1972    |
|    | 3,632,511 | Chien-Wei Liao | January 4, 1972    |
| 35 | 3,697,428 |                |                    |
|    | 3,725,441 | Murphy         | April 3, 1973      |
|    | 4,234,435 | Meinhardt      | November 18, 1980  |
| 40 | Re 26,433 | Le Suer        | August 6, 1968     |

(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:

| PATENT    | INVENTOR                           | ISSUE DATE                        |
|-----------|------------------------------------|-----------------------------------|
| 3,275,554 | vander Voort et al<br>Honnen et al | July 8, 1969<br>February 23, 1971 |
| 3,438,757 |                                    |                                   |
| 3,454,555 |                                    |                                   |
| 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:

| PATENT    | INVENTOR        | ISSUE DATE         |
|-----------|-----------------|--------------------|
| 2,459,112 | Oberright       | January 11, 1949   |
| 2,962,442 | Andress         | November 29, 1960  |
| 2,984,550 | Chamot          | May 16, 1961       |
| 3,036,003 | Verdol          | May 27, 1962       |
| 3,166,516 |                 |                    |
| 3,236,770 | Matson          | February 22, 1966  |
| 3,355,270 | Amick           | November 28, 1967  |
| 3,368,972 | Otto            | February 13, 1968  |
| 3,413,347 | Worrel          | November 26, 1968  |
| 3,442,808 | Traise          | May 6, 1969        |
| 3,448,047 | Traise          | June 3, 1969       |
| 3,454,497 | Wittner         | July 8, 1969       |
| 3,459,661 | Schlobohm       | August 5, 1969     |
| 3,461,172 |                 |                    |
| 3,493,520 | Verdol et al    | February 3, 1970   |
| 3,539,633 | Piasek et al    | November 10, 1970  |
| 3,558,743 | Verdol et al    | January 26, 1971   |
| 3,586,629 | Otto et al      | June 22, 1971      |
| 3,591,598 | Traise et al    | July 6, 1971       |
| 3,600,372 | Udelhofen et al | August 17, 1971    |
| 3,634,515 | Piasek et al    | January 11, 1972   |
| 3,649,229 |                 |                    |
| 3,697,574 | Piasek et al    | October 10, 1972   |
| 3,725,277 | Worrel          | April 3, 1973      |
| 3,725,480 | Traise et al    | April 3, 1973      |
| 3,726,882 | Traise et al    | April 10, 1973     |
| 3,980,569 | Pindar et al    | September 14, 1976 |

(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:

|    | PATENT    | INVENTOR      | ISSUE DATE         |
|----|-----------|---------------|--------------------|
|    | 3,036,003 | Verdol        | May 22, 1962       |
| 5  | 3,087,936 | Le Suer       | April 30, 1963     |
|    | 3,200,107 | Le Suer       | August 10, 1965    |
|    | 3,216,936 | Le Suer       | November 9, 1965   |
| 10 | 3,254,025 | Le Suer       | May 31, 1966       |
|    | 3,256,185 | Le Suer       | June 14, 1966      |
|    | 3,278,550 | Norman et al  | October 11, 1966   |
| 15 | 3,280,234 |               |                    |
|    | 3,281,428 | Le Suer       | October 25, 1966   |
|    | 3,282,955 | Le Suer       | November 1, 1966   |
|    | 3,312,619 | Dale          | April 4, 1967      |
| 20 | 3,366,569 | Norman et al  | January 30, 1968   |
|    | 3,367,943 |               |                    |
|    | 3,373,111 | Le Suer et al | March 12, 1968     |
| 25 | 3,403,102 | Le Suer       | September 24, 1968 |
|    | 3,442,808 | Traise et al  | May 6, 1969        |
|    | 3,455,831 |               |                    |
| 30 | 3,455,832 |               |                    |
|    | 3,493,520 | Verdol et al  | February 3, 1970   |
|    | 3,502,677 | Le Suer       | March 24, 1970     |
| 35 | 3,513,093 | Le Suer       | May 19, 1970       |
|    | 3,533,945 | Vogel         | October 13, 1970   |
|    | 3,539,633 | Piasek et al  | November 10, 1970  |
|    | 3,573,010 | Mehmedbasich  | March 30, 1971     |
| 40 | 3,579,450 | Le Suer       | May 18, 1971       |
|    | 3,591,598 | Traise        | July 6, 1971       |
|    | 3,600,372 |               |                    |
| 45 | 3,639,242 | Le Suer       | February 1, 1972   |
|    | 3,649,229 |               |                    |

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|-----------|--------------|------------------|
| 3,649,659 | Otto et al   | March 14, 1972   |
| 3,658,836 | Vineyard     | April 25, 1972   |
| 3,697,574 | Piasek et al | October 10, 1972 |
| 3,702,757 |              |                  |
| 3,703,536 |              |                  |
| 3,704,308 |              |                  |
| 3,708,422 | Swanson      | January 2, 1973  |

(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:

| PATENT    | INVENTOR | ISSUE DATE       |
|-----------|----------|------------------|
| 3,329,658 | Fields   | July 4, 1967     |
| 3,449,250 |          |                  |
| 3,519,565 | Coleman  | July 7, 1970     |
| 3,666,730 | Coleman  | May 30, 1972     |
| 3,687,849 | Abbott   | August 29, 1972  |
| 3,702,300 | Coleman  | November 7, 1972 |

As previously mentioned, the invention is concerned with additives for diesel lubricants. Generally, the lubricant compositions used in accordance with the invention comprise a major amount of an oil of lubricating viscosity and a minor amount of the manganese or other metallic compound of the present invention.

The term "minor amount" as used herein is intended to mean that when a composition contains a "minor amount" of a specific material that amount is less than 50% by weight of the composition.

The term "major amount" as used herein is intended to mean that when a composition contains a "major amount" of a specific material that amount is more than 50% by weight of the composition.

The amount of the metallic compound to the lubricant oil in the compositions used in accordance with this invention is such that the treated lubricant compositions have the metal present at 30 ppm to 500 ppm, preferably 35 ppm to 350 ppm, and most preferably 40 ppm to 150 ppm by weight of the composition.

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

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

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters, or the C<sub>13</sub>oxo acid diester of tetraethylene glycol.

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

Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butyl-phenyl)silicate, hexyl(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, trioxyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans and the like.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil.

Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, hydrotreating, hydrocracking, 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.

Most preferably, the oil used herein is a petroleum derived oil. Coincidentally, the greatest effects of the various metals used herein are found in petroleum derived oils.

The effect of soot related viscosity increase and viscosity rate increase on the lubricant may be retarded by periodically adding a portion of fresh lubricant treated with the metals according to the present invention. Thus, an initially untreated (metal) lubricant may enjoy the benefits herein by using a treated lubricant for replacement between oil changes. The metallic compound may also be added to the crankcase in the presence of a diluent oil wherein the metallic compound is present in a 1 to 25 fold excess (as the metal) over that normally found in the oil. In this manner, a diesel crankcase containing twenty to twenty-five liters of untreated oil is brought up to the correct metallic compound level by adding as little as one liter of additive.

The lubricant oil is typically utilized in the invention at 75% to 99.5% by weight of the composition, preferably about 80% to about 99% by weight. The diluent oils (lubricants) present as various additives are included in the above amounts. The dispersant as previously discussed is conveniently utilized at 0.05% to 20% by weight, preferably 0.1% to 15% by weight of the composition.

The diesel lubricating compositions utilized herein are preferably substantially free of lead, iron, aluminum or tin in any form. The absence of the aforementioned metals is desired because they are wear metals, or materials which normally comprise a portion of the engine. The presence of wear metals during analysis by a fleet owner usually indicates a problem of wear in the engine. Thus, wear metals are desirably not included in a lubricant as these materials reduce the reliability of the analytical methods used to detect wear. The metals described as being undesirable also have the potential to act as oxidation catalysts which can result in oil oxidation thus requiring premature oil changes.

The total base number of the diesel lubricant is typically between 0 and 25, preferably between 1 and 15. The total base number indicates that the lubricant is capable of withstanding changes toward acid build-up. Acid build-up causes increased corrosion and a higher base-number represents resistance to acid build-up.

In a preferred embodiment, the diesel lubricants used according to the present invention also contain at least one oil-soluble neutral or basic alkaline earth metal salt of at least one acidic organic compound. Such salt compounds generally are referred to as ash-containing detergents. The acidic organic compound may be at least one sulfur acid, carboxylic acid, phosphorus acid, phenol, salicylate or mixtures thereof.

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

The salts which are useful can be neutral or basic. The neutral salts contain an amount of alkaline earth metal which is just sufficient to neutralize the acidic groups present in the salt anion, and the basic salts contain an excess of the alkaline earth metal cation.

10 The amount of the alkaline earth metal salt included in the diesel lubricants of the present invention also may be varied over a wide range, and useful amounts can be readily determined by one skilled in the art. The salt functions as an auxiliary or supplemental detergent. The amount of the alkaline earth metal salt diesel lubricant of the invention may vary from about 0% to about 5% or more, preferably 0.5% to 4% by weight of the composition.

15 The present invention also contemplates the use of other additives in the diesel lubricant compositions. These other additives include such conventional additive types as anti-oxidants, extreme pressure agents, corrosion-inhibiting agents, pour point depressants, color stabilizing agents, anti-foam agents, and other such additive materials known generally to those skilled in the art of formulating diesel lubricants. Where anti-oxidants are employed, it is preferred that the anti-oxidant be of the amine type such as an alkylated aryl amine. Preferably, the t-butyl hindered phenolics are not employed in the present invention. If used, the hindered phenolic should be employed with a second anti-oxidant.

Extreme pressure agents and corrosion- and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, 25 sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium 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.

35 Many of the above-mentioned auxiliary extreme pressure agents and corrosion-oxidation inhibitors also serve as antiwear agents. Zinc dialkylphosphorodithioate compounds are a well known example.

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

45 Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in the following U. S. Patents:

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| PATENT    | INVENTOR | ISSUE DATE        |
|-----------|----------|-------------------|
| 2,387,501 | Reiff    | February 27, 1940 |
| 2,015,748 |          |                   |
| 2,655,479 |          |                   |
| 1,815,022 |          |                   |
| 2,191,498 |          |                   |
| 2,666,746 |          |                   |
| 2,721,877 | Wyman    | May 10, 1966      |
| 2,721,878 |          |                   |
| 3,250,715 |          |                   |

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

Viscosity improvers are typically included at 5% to 15% by weight of the composition. The viscosity improvers function to maintain more or less constant viscosity as the lubricant temperature is increased. Examples of viscosity improvers are hydrogenated styrene-isoprene copolymers; maleic anhydride styrene copolymers; olefin copolymers such as ethylene-propylene copolymers; styrene butadiene copolymers and homopolymers such as polybutylene.

The present invention will be further understood by a consideration of the following examples which are intended to be purely exemplary of the invention. Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the following.

#### EXAMPLE I

A fully formulated lubricant composition is prepared containing:

| COMPONENTS                                                                                                                                           | PARTS  |
|------------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| Mineral oil                                                                                                                                          | 92.45  |
| Viscosity Improver                                                                                                                                   | 0.68   |
| Basic Magnesium alkylated benzene sulfonate                                                                                                          | 0.77   |
| Dispersant                                                                                                                                           | 3.48   |
| Zinc salts of alkylated phosphorodithioic acids                                                                                                      | 1.43   |
| Anti-wear detergent                                                                                                                                  | 1.11   |
| Silicone anti-foam                                                                                                                                   | 0.001  |
| Antioxidant                                                                                                                                          | 0.08   |
| Manganese as its sulfonate from dialkylated benzene having an average alkyl benzene molecular weight between 300 and 380 reported as manganese metal | 50 ppm |

The product of Example I gave a Mack T-7 test result slope of 0.018 between 100 and 150 hours of operation. A passing slope value under the current Mack T-7 test is 0.04 or less. The same formulation without the manganese gave a test value of 0.16.

**EXAMPLE II**

A fully formulated lubricant composition is prepared containing:

| COMPONENTS                                                              | PARTS  |
|-------------------------------------------------------------------------|--------|
| Mineral oil                                                             | 92.45  |
| Viscosity Improver                                                      | 0.68   |
| Basic Magnesium alkylated benzene sulfonate                             | 0.77   |
| Dispersant                                                              | 3.48   |
| Zinc salts of alkylated phosphorodithioic acids                         | 1.43   |
| Anti-wear detergent                                                     | 1.11   |
| Silicone anti-foam                                                      | 0.001  |
| Antioxidant                                                             | 0.08   |
| Manganese oxide, hydroxide, and carboxylate (neodecanoate) as manganese | 40 ppm |

This formulation gave a Mack T-7 slope test result of 0.035 where 0.04 is passing. The test slope value in the absence of the manganese is 0.16.

**EXAMPLE III**

A fully formulated lubricant composition is prepared containing:

| COMPONENTS                                      | PARTS  |
|-------------------------------------------------|--------|
| Mineral oil                                     | 92.45  |
| Viscosity Improver                              | 0.68   |
| Basic Magnesium alkylated benzene sulfonate     | 0.77   |
| Dispersant                                      | 3.48   |
| Zinc salts of alkylated phosphorodithioic acids | 1.43   |
| Anti-wear detergent                             | 1.11   |
| Silicone anti-foam                              | 0.001  |
| Antioxidant                                     | 0.08   |
| Cobalt as a naphthenate                         | 50 ppm |

The cobalt containing formulation gives a Mack T-7 test slope value of 0.068 and shows an improvement of greater than 50% over the formulations not containing cobalt. The viscosity increase in the lubricant is 58% greater over the interval of 100 to 150 hours in the absence of cobalt.

**EXAMPLE IV**

A fully formulated diesel lubricant composition is prepared containing:

| COMPONENTS                                                                 | PARTS  |
|----------------------------------------------------------------------------|--------|
| Mineral oil                                                                | 92.45  |
| Viscosity Improver                                                         | 0.68   |
| Basic Magnesium alkylated benzene sulfonate                                | 0.77   |
| Dispersant                                                                 | 3.48   |
| Zinc salts of alkylated phosphorodithioic acids                            | 1.43   |
| Anti-wear detergent                                                        | 1.11   |
| Silicone anti-foam                                                         | 0.001  |
| Antioxidant                                                                | 0.08   |
| Titanium (as titanium) in the form of titanium isopropoxide organic adduct | 50 ppm |

The Mack T-7 test results on the titanium compound shows a slope value of 0.026. The viscosity increase over the base line is 182% when titanium is not employed.

**EXAMPLE V**

A fully formulated lubricant composition is prepared containing:

| COMPONENTS                                      | PARTS |
|-------------------------------------------------|-------|
| Mineral oil                                     | 92.45 |
| Viscosity Improver                              | 0.68  |
| Basic Magnesium alkylated benzene sulfonate     | 0.77  |
| Dispersant                                      | 3.48  |
| Zinc salts of alkylated phosphorodithioic acids | 1.43  |
| Anti-wear detergent                             | 1.11  |
| Silicone anti-foam                              | 0.001 |
| Antioxidant                                     | 0.08  |

This example utilizes manganese salicylate at 450 ppm manganese.

**Claims**

1. Use of an oil-soluble or oil-dispersible metallic compound wherein the metal is selected from manganese, titanium, cobalt and mixtures thereof, for retarding soot related viscosity rate increase of a lubricant in a diesel engine lubricating system prone to soot build-up, wherein the metallic compound is present as a metal at 30 ppm to 500 ppm of the lubricant.
2. Use according to claim 1 wherein the lubricant comprises an oil of lubricating viscosity which is present at from 75% to 99.5% by weight of the lubricant.
3. Use according to either of claims 1 and 2 wherein the metallic compound contains manganese which is present as the metal at 30 ppm to 500 ppm of the lubricant.
4. Use according to any preceding claim wherein the metallic compound is present as the metal at 35 ppm to 350 ppm of the lubricant.
5. Use according to any preceding claim wherein the lubricant has a total base number of from 0 to 25.
6. Use according to any preceding claim wherein the lubricant is substantially free of lead.
7. Use according to any preceding claim wherein the metallic compound is a sulfonate, carboxylate, phosphonate, salicylate, phenate or naphthenate.
8. Use according to claim 7 wherein the carboxylate is derived from a fatty acid having from 6 to 30 carbon atoms per carboxyl group.
9. Use according to any preceding claim wherein the lubricant additionally contains viscosity improver at 5% to 15% by weight of the lubricant.
10. Use according to any preceding claim wherein the lubricant further contains a dispersant.
11. Use according to claim 10 wherein the dispersant is selected from phosphorus-containing olefin polymers, amine dispersants, Mannich dispersants and alkali metal and alkaline earth metal salts of carboxylic acids and organic phosphorous acids.
12. Use according to either of claims 10 and 11 wherein the dispersant is present at 0.05% to 20% by the weight of the lubricant.
13. Use according to any preceding claim wherein the lubricant also contains a zinc compound.

**EXAMPLE V**

A fully formulated lubricant composition is prepared containing:

| COMPONENTS                                      | PARTS |
|-------------------------------------------------|-------|
| Mineral oil                                     | 92.45 |
| Viscosity Improver                              | 0.68  |
| Basic Magnesium alkylated benzene sulfonate     | 0.77  |
| Dispersant                                      | 3.48  |
| Zinc salts of alkylated phosphorodithioic acids | 1.43  |
| Anti-wear detergent                             | 1.11  |
| Silicone anti-foam                              | 0.001 |
| Antioxidant                                     | 0.08  |

This example utilizes manganese salicylate at 450 ppm manganese.

**Claims**

1. Use of an oil-soluble or oil-dispersible metallic compound wherein the metal is selected from manganese, titanium, cobalt and mixtures thereof, for retarding soot related viscosity rate increase of a lubricant in a diesel engine lubricating system prone to soot build-up, wherein the metallic compound is present as a metal at 30 ppm to 500 ppm of the lubricant.
2. Use according to claim 1 wherein the lubricant comprises an oil of lubricating viscosity which is present at from 75% to 99.5% by weight of the lubricant.
3. Use according to either of claims 1 and 2 wherein the metallic compound contains manganese which is present as the metal at 30 ppm to 500 ppm of the lubricant.
4. Use according to any preceding claim wherein the metallic compound is present as the metal at 35 ppm to 350 ppm of the lubricant.
5. Use according to any preceding claim wherein the lubricant has a total base number of from 0 to 25.
6. Use according to any preceding claim wherein the lubricant is substantially free of lead.
7. Use according to any preceding claim wherein the metallic compound is a sulfonate, carboxylate, phosphonate, salicylate, phenate or naphthenate.
8. Use according to claim 7 wherein the carboxylate is derived from a fatty acid having from 6 to 30 carbon atoms per carboxyl group.
9. Use according to any preceding claim wherein the lubricant additionally contains viscosity improver at 5% to 15% by weight of the lubricant.
10. Use according to any preceding claim wherein the lubricant further contains a dispersant.
11. Use according to claim 10 wherein the dispersant is selected from phosphorus-containing olefin polymers, amine dispersants, Mannich dispersants and alkali metal and alkaline earth metal salts of carboxylic acids and organic phosphorous acids.
12. Use according to either of claims 10 and 11 wherein the dispersant is present at 0.05% to 20% by the weight of the lubricant.
13. Use according to any preceding claim wherein the lubricant also contains a zinc compound.



## Patentansprüche

1. Verwendung einer öllöslichen oder in Öl dispergierbaren Metallverbindung, wobei das Metall ausgewählt ist aus Mangan, Titan, Kobalt und deren Gemischen, zur Verzögerung der durch Ruß auftretenden Erhöhung der Viskositätsrate eines Schmiermittels in einem Dieselmotor-Schmiermittelsystem, das zur Rußbildung neigt, wobei die Metallverbindungen als Metall in einer Menge von 30ppm bis 500ppm des Schmiermittels vorliegen.
2. Verwendung nach Anspruch 1, wobei das Schmiermittel ein Öl mit Schmierviskosität umfaßt, das in einer Menge von 75 bis 99.5 Gew.-% des Schmiermittels vorliegt.
3. Verwendung nach Anspruch 1 oder 2, wobei die Metallverbindung Mangan enthält, das als Metall in einer Menge von 30ppm bis 500 ppm des Schmiermittels vorliegt.
4. Verwendung nach einem der vorstehenden Ansprüche, wobei die Metallverbindung als Metall in einer Menge von 35ppm bis 350ppm vorliegt.
5. Verwendung nach einem der vorstehenden Ansprüche, wobei das Schmiermittel eine Gesamt-Basenzahl von 0 bis 25 hat.
6. Verwendung nach einem der vorstehenden Ansprüche, wobei das Schmiermittel im wesentlichen kein Blei enthält.
7. Verwendung nach einem der vorstehenden Ansprüche, wobei die Metallverbindung ein Sulfonat, Carboxylat, Phosphonat, Salicylat, Phenolat oder Naphthenat ist.
8. Verwendung nach Anspruch 7, wobei das Carboxylat sich von einer Fettsäure mit 6 bis 30 C-Atomen pro Carboxyl-Gruppe ableitet.
9. Verwendung nach einem der vorstehenden Ansprüche wobei das Schmiermittel zusätzlich ein Viskositätsverbesserer in einer Menge von 5 bis 15 Gew.-% des Schmiermittels enthält.
10. Verwendung nach einem der Ansprüche wobei das Schmiermittel zusätzlich ein Dispersant enthält.
11. Verwendung nach Anspruch 10, wobei das Dispersant ausgewählt ist aus Phosphor-enthaltenden Olefinpolymeren, Amin-Dispersants Mannich-Dispersants und Alkali- und Erdalkalimetallsalzen von Carbonsäuren und organischen Phosphorsäuren.
12. Verwendung nach Anspruch 10 oder 11, wobei das Dispersant in einer Menge von 0.05 bis 20 Gew.-% des Schmiermittels vorliegt.
13. Verwendung nach einem der vorstehenden Ansprüche, wobei das Schmiermittel zusätzlich eine Zinkverbindung enthält.

## Revendications

1. Utilisation d'un composé métallique soluble dans l'huile ou dispersible dans l'huile, dans laquelle le métal est choisi parmi le manganèse, le titane, le cobalt et des mélanges de ceux-ci afin de retarder l'accroissement du taux de viscosité, dû à la suie, d'un lubrifiant dans un système de lubrification de moteur Diesel, sujet à la production de suie, le composé métallique étant présent, sous forme de métal, à raison de 30 ppm à 500 ppm dans le lubrifiant.
2. Utilisation selon la revendication 1, dans laquelle le lubrifiant comporte une huile de viscosité lubrifiante, qui est présente à raison de 75 % à 99,5 % en poids de lubrifiant.
3. Utilisation selon l'une quelconque des revendications 1 et 2, dans laquelle le composé métallique contient du manganèse qui est présent, en tant que métal, à raison de 30 ppm à 500 ppm dans le lubrifiant.



4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le composé métallique est présent, en tant que métal, à raison de 35 à 350 ppm dans le lubrifiant.
- 5 5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le lubrifiant présente un indice de base total de 0 à 25.
6. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le lubrifiant est pratiquement exempt de plomb.
- 10 7. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le composé métallique est un sulfonate, un carboxylate, un phosphonate, un salicylate, un phénate ou un naphtéate.
8. Utilisation selon la revendication 7, dans laquelle le carboxylate est dérivé d'un acide gras ayant de 6 à 30 atomes de carbone par groupe de carboxyle.
- 15 9. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le lubrifiant renferme en outre un agent améliorant la viscosité à raison de 5 % à 15 % en poids de lubrifiant.
- 20 10. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le lubrifiant renferme en outre un agent dispersant.
- 25 11. Utilisation selon la revendication 10 dans laquelle l'agent dispersant est choisi parmi les polymères oléfiniques renfermant du phosphore, des dispersants aminés, des dispersants de Mannich et des sels de métaux alcalins et de métaux alcalino-terreux d'acides carboxyliques et des acides phosphoreux organiques.
12. Utilisation selon l'une quelconque des revendications 10 et 11, dans laquelle le dispersant est présent à raison de 0,05 % à 20 % en poids dans le lubrifiant.
- 30 13. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le lubrifiant renferme également un composé du zinc.

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