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## ⑫ EUROPEAN PATENT APPLICATION

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(71) Applicant: **EDWIN COOPER INC., 1525 South Broadway, St. Louis Missouri 63104 (US)**

(72) Inventor: **Papay, Andrew George, 897 Rustic Manor Circle, Manchester, Missouri 63011 (US)**
Inventor: **O'Brien, Joseph Peter, 713 West Jewell Avenue, Kirkwood, Missouri, 63122 (US)**

(74) Representative: **Allard, Susan Joyce et al, BOULT, WADE & TENNANT 27 Furnival street, London EC4A 1PQ (GB)**

## (54) Oil-soluble friction-reducing additive, process for the preparation thereof, and lubricating oil or fuel composition containing the additive.

(57) Additives are provided for lubricants, or fuels for internal combustion engines. They are oil-soluble aliphatic hydrocarbyl-substituted succinimide or succinamide materials, wherein the hydrocarbyl group contains about 12 to 36 carbon atoms and is preferably derived from an isomerized straight chain α-olefin.

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ACTORUM AG

# OIL-SOLUBLE FRICTION-REDUCING ADDITIVE, PROCESS FOR THE PREPARATION THEREOF, AND LUBRICATING OIL OR FUEL COMPOSITION CONTAINING THE ADDITIVE

This invention is in the field of lubricants and lubricant additives. More particularly, the invention deals with additives to lubricants especially for crankcase use for internal combustion engines, which provide a reduction of friction of the operating engine.

In order to conserve energy, automobiles are now being engineered to give improved gasoline mileage compared to those in recent years. This effort is of great urgency in the United States in view of regulations which compel auto manufacturers to achieve prescribed gasoline mileage. These regulations are to conserve crude oil. In an effort to achieve the required mileage, new cars are being downsized and made much lighter. However, there are limits in this approach beyond which the cars will not accommodate a typical family.

Another way to improve fuel mileage is to reduce engine friction. The present invention is concerned with this latter approach.

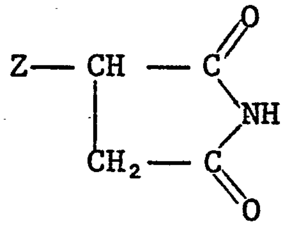
The present invention utilizes the finding that a material which is an oil soluble, $C_{12-36}$ aliphatic hydrocarbyl succinimide or succinamide provides a friction reducing effect where it is incorporated in lubricating oil. Preferably, the aliphatic hydrocarbon group is derived from a linear $\alpha$-olefin which has been isomerized to form a mixture of internal olefins. The additive can also be used in the engine fuel.

A preferred embodiment of the invention is a lubricating oil composition containing a friction-reducing amount of an additive selected from the group consisting of oil soluble aliphatic hydrocarbon-substituted succinimide and succinamide and mixtures thereof wherein said hydrocarbon substituent contains about 12 to 36 carbon atoms.

The aliphatic substituent on the succinic group can be any aliphatic hydrocarbon group containing about 12 to 36 carbon atoms including alkyl, alkenyl and polyunsaturated hydrocarbon groups. Examples of the above additives include:

_n_-dodecynyl succinimide
1-methyltridecyl succinimide
2-ethyltetradecyl succinimide
_n_-hexadecenyl succinimide
_n_-octadecyl succinimide
_n_-octadecenyl succinimide
1-methyleicosyl succinimide
_n_-docosenyl succinimide
4-ethyltriacontyl succinimide
_n_-hexadecenyl succinimide
_n_-dodecenyl succinamide
2-ethyltetradecyl succinamide
_n_-octadecyl succinamide
_n_-octadecenyl succinamide.

In a preferred embodiment the aliphatic hydrocarbon group is bonded to the succinic group at a secondary carbon atom. These compounds have the formula:



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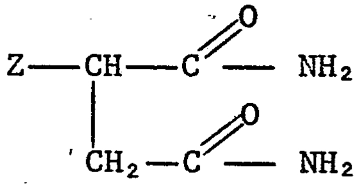

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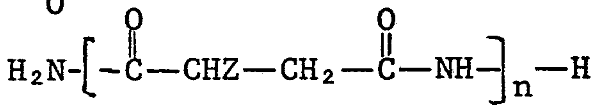
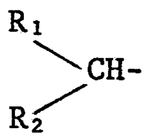


$$H_2N\text{-}\left[-\overset{\displaystyle O}{\overset{\|}{C}}-CHZ-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NH-\right]_n-H$$

wherein n is a small integer from 2 to about 4 and Z is the group:



wherein $R_1$ and $R_2$ are independently selected from the group consisting of branched and straight chain hydrocarbon groups containing 1 to about 34 carbon atoms such that the total number of carbon atoms in $R_1$ and $R_2$ is about 11 to 35. Examples of these additives are:

1-ethyltetradecyl succinimide
1-methylpentadecenyl succinimide
1,2-dimethyl octadecenyl succinamide
1-methyl-3-ethyl dodecenyl succinimide
1-decyl-2-methyl dotriacontyl succinimide.

In a highly preferred embodiment $R_1$ and $R_2$ are straight chain aliphatic hydrocarbon groups. These additives have improved solubility in lubricating oil. Examples of these additives are:

1-methylpentadecyl succinimide
1-propyltridecenyl succinimide
1-pentyltridecenyl succinimide
1-tridecylpentadecenyl succinimide
1-tetradecyleicosenyl succinimide.

The above highly preferred additives are preferably made from linear α-olefins containing about 12 to 36 carbon atoms by isomerizing the α-olefins to form a mixture of internal olefins and reacting this mixture of internal olefins with maleic acid, anhydride or ester forming an intermediate and reacting the intermediate with ammonia to form amide, imide, or mixtures thereof.

Additives made from isomerized linear α-olefins have greatly improved oil solubility compared with additives made with linear α-olefins.

Isomerization of the linear α-olefin can be carried out using conventional methods. One suitable method is to heat the linear α-olefin with an acidic catalyst. Especially useful acid catalysts are the sulfonated styrene-divinylbenzene copolymers. Such catalysts are commercially available and are conventionally used as cation exchange resins. In the present method they are used in their acid form. Typical resins are Amberlyst 15, XN-1005 and XN-1010 (registered trademarks) available from Rohm and Haas Company. Use of such resins for isomerizing linear α-olefins is described in U. S. 4,108,889, incorporated herein by reference.

The method by which the present additives are made are illustrated by the following examples.

Example 1

In a reaction vessel was placed 185 grams of octadecenyl succinic anhydride. This was melted by heating to 60° C. and $NH_3$ was injected. An exothermic reaction proceeded raising the temperature to 160° C. After the reaction ceased, the product was heated to 180° C. under about 737 mm (29 in.) Hg vacuum to remove volatiles. The product was octadecenyl succinimide.

Example 2

In a reaction vessel was placed 1000 grams of linear α-octadecene. To this was added 187 grams Amberlyst 15 (5 percent moisture). The mixture was stirred under nitrogen and heated at 120° C. for 3 hours. The isomerized product contained 3.6 weight percent olefin dimer and the balance was internal $C_{18}$ olefin. The product was separated from the resin.

In a second reaction vessel was placed 504 grams of the above isomerized $C_{18}$ olefin and 300 ml heptane. The heptane was distilled out under vacuum to remove water. Then 2.4 grams of tri-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-mesitylene stabilizer was added. The mixture was heated under nitrogen to 225° C. Then 160 grams of molten maleic anhydride was slowly added over a 2.5-hour period. The mixture was stirred at 225° C. for two more hours and then unreacted maleic anhydride was distilled out by pulling vacuum to 762 mm (30 in.) Hg while holding the reaction mixture at 200° C. The product was principally secondary $C_{18}$ alkylene succinic anhydride.

In a separate reaction vessel was placed 532.5 grams of the above isomerized octadecenyl succinic anhydride. This was heated under nitrogen to 165° C. and then ammonia was injected causing the temperature to rise to 180° C.

Ammonia injection was continued until exotherm stopped. The mixture was heated at 170° C. under vacuum to remove water yielding isomerized octadecenyl succinimide.

Example 3

In a reaction vessel was placed 1005 grams of linear α-eicosene and 187 grams of Amberlyst 15 (5 percent moisture). The mixture was heated under nitrogen at 110° to 125° C. for 6 hours. The product was internally unsaturated eicosene containing 3.3 percent eicosene dimer.

In a separate reaction vessel was placed 560 grams of the above isomerized eicosene and 200 ml heptane. The heptane was distilled out to dry the eicosene. At 140° C., 3.1 grams of tri-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitylene stabilizer was added and the mixture heated to 210° C. Over a 2.5-hour period, 156.8 grams of maleic anhydride was added at about 225° C. Following this, unreacted maleic anhydride was distilled out under vacuum at 210° C. leaving isomerized eicosenyl succinic anhydride.

In another reaction vessel was placed 570 grams of the above isomerized eicosenyl succinic anhydride. This was heated to 160° C. and ammonia injection started. The temperature rose to 175° C. Ammonia injection was continued at 175° C. until the temperature dropped. Then 762 mm (30 in.) Hg vacuum was slowly applied to distill out water and ammonia. Additional ammonia was injected to be sure no anhydride remained. There was no further reaction so this ammonia was stripped out at 762 mm (30 in.) Hg vacuum at 170° C. yielding isomerized eicosenyl succinimide.

Example 4

In a reaction vessel was placed 1100 grams of linear $C_{16}$-$C_{18}$ α-olefin mixture. The olefin mixture was isomerized following the procedure in Example 3.

In a separate vessel was placed 485 grams (2 moles) of the above isomerized olefin. This was heated at 100° C. under 30 inches Hg vacuum to remove water. To it was then added 2.4 grams tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-mesitylene. The mixture was heated under nitrogen to 225° C. and then 152 grams of molten maleic anhydride was added over a 3-hour period. The mixture was stirred 30 minutes at 225° C. and an additional 50 grams of maleic anhydride was added. This mixture was stirred 30 minutes at 225° C. following which unreacted maleic anhydride was distilled out at 200° C. under 762 mm (30 in.) Hg vacuum.

In a separate reaction vessel was placed 598 grams of the above isomerized $C_{16}$-$C_{18}$ alkenyl succinic anhydride. Ammonia injection was started at 140° C. raising the temperature to 145° C. Ammonia injection was continued at 130° C. until no further ammonia was adsorbed. The mixture was then heated to 180° C. to distill out water and ammonia yielding isomerized $C_{16}$-$C_{18}$ alkenyl succinimide.

The additives are added to the lubricating oil in an amount which reduces the friction of the engine operating with the oil in the crankcase. A useful concentration is about 0.05 to 3 weight percent. A more preferred range is about 0.1 to 1.0 weight percent.

From the above it can be seen that the present invention provides an improved crankcase lubricating oil. Accordingly, an embodiment of the invention is an improved motor oil composition formulated for use as a crankcase lubricant in an internal combustion engine wherein the improvement comprises including in the crankcase oil an amount sufficient to reduce fuel consumption of the engine of the friction-reducing additive herein described.

In a highly preferred embodiment such improved motor oil also contains an ashless dispersant and an alkaline earth metal salt of a petroleum sulfonic acid or an alkaryl sulfonic acid (e.g., alkylbenzene sulfonic acid).

The additives can be used in mineral oil or in synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine. Crankcase lubricating oils have a viscosity up to about 80 SUS at 100° C. (210° F.).

Mineral oils include those of suitable viscosity refined from crude oil from all sources including Gulfcoast, midcontinent, Pennsylvania, California, Alaska and the like. Various standard refinery operations can be used in processing the mineral oil.

Synthetic oil includes both hydrocarbon synthetic oil and synthetic esters. Useful synthetic hydrocarbon oils including liquid polymers of α-olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of $C_{6-12}$ α-olefins such as α-decene trimer. Likewise, alkylbenzenes of proper viscosity can be used, such as didodecylbenzene.

Useful synthetic esters include the esters of both monocarboxylic acid and polycarboxylic acid as well as monohydroxy alkanols and polyols. Typical examples are didocecyl adipate, trimethylol propane tripelargonate, pentaerythritol tetracaproate, di(2-ethylhexyl)adipate, dilauryl sebacate and the like. Complex esters prepared from mixtures of mono- and dicarboxylic acid and mono- and polyhydroxyl alkanols can also be used.

Blends of mineral oil with synthetic oil are particularly useful. For example, blends of 5 to 25 weight percent hydrogenated α-decene trimer with 75 to 95 weight percent 150 SUS 38° C. (100° F.) mineral oil results in an excellent lubricant. Likewise, blends of about 5 to 25 weight percent di(2-ethylhexyl)adipate with mineral oil of proper viscosity results in a superior lubricating oil. Also blends of synthetic hydrocarbon oil with synthetic esters can be used. Blends of mineral oil with synthetic oil are especially useful when preparing low viscosity oil (e.g., SAE 5W 20) since they permit these low viscosities without contributing excessive volatility.

The more preferred lubricating oil compositions include zinc dihydrocarbyldithiophosphate (ZDDP) in combination with the present additives. Both zinc dialkyldithiophosphates and zinc dialkaryldithiophosphates as well as mixed alkyl-aryl dithiophosphates can be used. Examples of alkyl-type ZDDP are those in which the hydrocarbyl groups are a mixture of isobutyl and isoamyl alkyl groups. Zinc di-(nonylphenyl)-dithiophosphate is an example of an aryl-type ZDDP. Good results are achieved using sufficient zinc dihydrocarbyldithiophosphate to provide about 0.01 to 0.5 weight percent zinc. A preferred concentration supplies about 0.05 to 0.3 weight percent zinc.

Another additive used in the oil compositions are the alkaline earth metal petroleum sulfonate or alkaline earth metal alkaryl sulfonates. Examples of these are calcium petroleum sulfonates, magnesium petroleum sulfonates, barium alkaryl sulfonates, calcium alkaryl sulfonates or magnesium alkaryl sulfonates. Both the neutral and the overbased sulfonates having base numbers up to about 400 can be beneficially used. These are used in an amount to provide about 0.05 to 1.5 weight percent alkaline earth metal and more preferably about 0.1 to 1.0 weight percent.

Viscosity index improvers can be included such as the polyalkylmethacrylate type or the ethylene-propylene copolymer type. Likewise, styrene-diene VI improvers can be used. Alkaline earth metal salts of phosphosulfurized polyisobutylene are useful. Preferred crankcase oils also contain an ashless dispersant such as the polyolefin succinamides and succinimides of polyethylene polyamines such as tetraethylenepentamine. The polyolefin succinic substituent is preferably a polyisobutene group having a molecular weight of from about 800 to 5,000. Such ashless dispersants are more fully described in U. S. 3,172,892 and U. S. 3,219,666 incorporated herein by reference.

Other useful ashless dispersants include the Mannich condensation products of polyolefin-substituted phenols, formaldehyde and polyethylene polyamine. Preferably, the polyolefin phenol is a polyisobutylene-substituted phenol in which the polyisobutylene group has a molecular weight of from about 800 to 5,000. The preferred polyethylene polyamine is tetraethylene pentamine. Such Mannich ashless dispersants are more fully descirbed in U. S. 3,368,972; U. S. 3,413,347; U. S. 3,442,808; U. S. 3,448,047; U. S. 3,539,633; U. S. 3,591,598; U. S. 3,600,372; U. S. 3,634,515; U. S. 3,697,574; U. S. 3,703,536; U. S. 3,704,308; U. S. 3,725,480; U. S. 3,726,882; U. S. 3,736,357; U. S. 3,751,365; U. S. 3,756,953; U. S. 3,793,202; U. S. 3,798,165; U. S. 3,798,247 and U. S. 3,803,039.

The friction-reducing additives of this invention are also useful in fuel compositions. Fuel injected or inducted into a combustion chamber wets the walls of the cylinder. Fuels containing a small amount of the present additive reduce the friction due to the piston rings sliding against the cylinder wall.

The additives can be used in both diesel fuel and gasoline used to operate internal combustion engines. Fuels containing about 0.001 to 0.25 weight percent of the friction-reducing additives can be used.

Fuels used with the invention can contain any of the additives conventionally added to such fuels. In the case of gasoline it can include dyes, antioxidants, detergents, antiknocks (e. g., tetraethyllead, methylcyclopentadienylmanganese tricarbonyl, rare earth metal chelates, methyl tert-butylether and the like). In the case of diesel fuels the compositions can include pour point depressants, detergents, ignition improvers (e.g., hexylnitrate) and the like.

Tests were conducted using a 1977 U. S. production automobile. These were shortened versions of the Federal City EPA cycle. This is referred to as the "Hot 505" cycle. It consists of the first 3.6 miles (5.8 km) of the Federal EPA City cycle started with a warmed-up engine instead of a cold engine. The car with a fully formulated

SE grade oil in its crankcase is operated on a chassis dynamometer for about one hour at about 88 km/hr. (55 mph) to stabilize oil temperature. It is then run through four consecutive "Hot 505" cycles measuring fuel economy of the base oil. Results of the four cycles are averaged. Then one-half of the base oil is drained from the crankcase and replaced with the same base oil containing a double dose of the test additive. The car is then run at about 88 km/hr. (55 mph) for about one hour to again stabilize temperature. A second series of four consecutive "Hot 505" cycles is run to measure initial fuel economy of the base oil containing the test additive. The car is then run about 805 km (500 miles) at constant speed of about 88 km/hr. (55 mph). Then a third series of four consecutive "Hot 505" cycles are run to measure fuel economy after about 805 km (500 miles) operation on the oil containing the test additive. The crankcase is then drained hot and filled with flushing oil which is run for a short time and then drained. The crankcase is then filled with the base oil which is run for a short time and then drained. The crankcase is then filled a second time with a base oil. This is run about one hour at about 88 km/hr. (55 mph) to a stable temperature. Then a fourth series of four consecutive "Hot 505" cycles are run measuring fuel economy. This gives a second base line thus bracketing the test carried out with the friction additive between two base line tests.

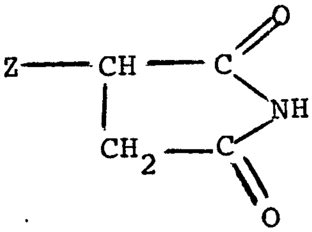
The following table shows the percent improvement in fuel economy over the base oil obtained using 1 weight percent of the friction-reducing additive.

| Additive | Percent Gain in Fuel Ecomony | | |
|---|---|---|---|
| | Initial | About 805 km (500 miles) | Average |
| Isomerized $C_{16-18}$ alkenyl succinimide | 1.6 | 0.9 | 1.3 |

The reduction in fuel consumption though small is significant.

CLAIMS

1. An oil-soluble friction-reducing additive which comprises at least one compound having the structure:



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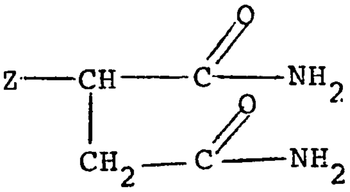

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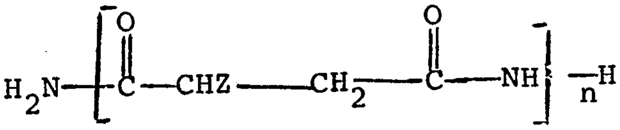
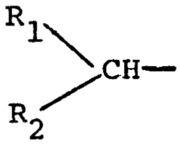


$$H_2N-\left[\overset{O}{\overset{\|}{C}}-CHZ-CH_2-\overset{O}{\overset{\|}{C}}-NH\right]_n-H$$

wherein n is an integer of from 2 to 4 and wherein Z has the structure:



wherein $R_1$ and $R_2$ are each independently straight or branched chain hydrocarbon groups containing from 1 to 34 carbon atoms such that the total number of carbon atoms in the groups $R_1$ and $R_2$ is from 11 to 35.

2. An oil-soluble friction-reducing additive as claimed in claim 1 wherein $R_1$ and $R_2$ are straight chain aliphatic hydrocarbon groups having a total of from 15 to 21 carbon atoms.

3. An oil-soluble friction reducing additive as claimed in claim 1 which is 1-methylpentadecyl succinimide, 1-propyltridecenyl succinimide, 1-pentyltridecenyl succinimide, 1-tridecylpentadecenyl succinimide or 1-tetradecyleicosenyl succinimide.

4. A process for the preparation of an oil-soluble additive as claimed in claim 1 which process comprises (a) isomerizing the olefinic double bond of a linear α-olefin or a mixture thereof containing from 12 to 36 carbon atoms to obtain a mixture of internal olefins, (b) reacting the mixture of internal olefins with maleic acid, anhydride or ester to obtain an intermediate hydrocarbon-substituted succinic acid, anhydride or ester and (c) reacting the intermediate with ammonia to form an amide, imide or a mixture thereof.

5. A process as claimed in claim 4 wherein the α-olefin consists mainly of linear α-tetradecene, linear α-hexadecene, linear α-octadecene or linear α-eicosene.

6. A process as claimed in claim 4 or claim 5 wherein the isomerization of the linear α-olefin is carried out by heating the linear α-olefin with an acidic catalyst.

7. A lubricating oil or fuel composition which contains a friction-reducing amount of an additive which is an oil-soluble aliphatic hydrocarbon-substituted succinimide or succinamide, or mixtures thereof, wherein the hydrocarbon substituent contains from 12 to 36 carbon atoms, or an additive as claimed in any one of claims 1 to 3 or whenever prepared by a process as claimed in any one of claims 4 to 6.

8. A lubricating oil or fuel composition as claimed in claim 7 wherein the additive is tetradecenyl succinimide, hexadecenyl succinimide, octadecenyl succinimide or eicosenyl succinimide.

9. A lubricating oil composition as claimed in claim 7 or claim 8 wherein the additive is contained therein in an amount of from 0.05 to 3 weight percent.

10. A fuel composition as claimed in claim 7 or claim 8 wherein the additive is contained therein in an amount of from 0.001 to 0.25 weight percent.

European Patent Office

# EUROPEAN SEARCH REPORT

0020037

Application number
EP 80 30 1487

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| X | GB - A - 1 111 837 (GAF)<br>* Claim 1; page 2, lines 40-180; page 5, lines 67-73 *<br>-- | 1-3,7,8 |
| X | US - A - 3 382 172 (W. LOWE)<br>* Column 1, lines 40-68; column 2, line 46 - column 3, line 1 *<br>-- | 4-6 |
| A | US - A - 3 655 351 (E.J. JAMIESON) | |
| A | GB - A - 877 845 (MOBIL OIL)<br>---- | |

☒ The present search report has been drawn up for all claims

CLASSIFICATION OF THE APPLICATION (Int. Cl. $^3$)

C 10 M 1/36
3/30
C 10 L 1/22
C 07 C 103/14
C 07 D 207/40

TECHNICAL FIELDS SEARCHED (Int.Cl. $^3$)

C 10 M 1/36
3/30
C 10 L 1/22
C 07 C 103/14
C 07 D 207/40

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 03.09.1980 | ROTSAERT |

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