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(54) Lubricating oil composition containing combination of succinimide and mannich base dispersants.

(57) Effective prevention of low temperature sludge formation and significantly reduced wear is obtained utilizing a lubricating oil composition having a combination dispersant of a hydrocarbon-substituted succinimide and a Mannich condensation product.

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BACKGROUND OF THE INVENTION

The present invention relates to lubricating compositions comprising a major portion of a lubricating oil and a minor portion of a dispersant. More particularly, this invention relates to dispersants comprising a combination of a hydrocarbon-substituted succinimide and a Mannich condensation product of a hydrocarbon-substituted phenol, an amine and formaldehyde.

Dispersants prepared from a hydrocarbon-substituted succinic acid or anhydride and a polyamine are well known. Representative patents include U.S. Patent Nos. 4,234,435 and 4,873,004. See also U.S. Patent Nos. 3,172,892 and 3,219,666.

Dispersants prepared from Mannich condensation products of a hydrocarbon-substituted phenol, an amine and formaldehyde are also well known. See, for example, U.S. Patent Nos. 3,413,347; 3,725,277; 3,368,972; and 3,798,165.

U.S. Patent No. 4,426,305 discloses lubricating oil compositions which include a combination of a boronated hydrocarbon-substituted succinic amide-imide/ester of an oxyalkylated amine and a Mannich condensation product, which is at least partially boronated, of a hydrocarbon-substituted phenol, an amine and formaldehyde. Such combination gives a better piston varnish rating than either individual component used at the same or even greater total concentration.

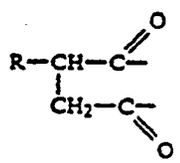
SUMMARY OF THE INVENTION

It has now been discovered that effective prevention of low temperature sludge formation can be obtained utilizing a dispersant comprising the combination of a non-boronated hydrocarbon-substituted succinimide dispersant and a Mannich condensation product dispersant.

DETAILED DESCRIPTION OF THE INVENTION

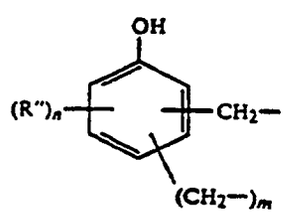
A preferred embodiment of the invention is a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor dispersant amount of a combination of dispersants comprising

(A) a succinimide dispersant having in its structure at least one aliphatic hydrocarbon-substituted succinoyl group represented by the formula



wherein R is an aliphatic hydrocarbon group having a number average molecular weight of from about 700 to about 5,000 said succinoyl group being bonded to a nitrogen atom of polyethylene amine to form an amide and/or imide, the molar proportion of said succinoyl group to said amine ranging from about 1.5:1 to about 2.2:1; and

(B) a Mannich dispersant having in its structure an aliphatic hydrocarbon-substituted phenolic group represented by the formula



wherein R″ is an aliphatic hydrocarbon group containing from 1 to about 500 carbon atoms and n is 1 or 2, m is 0 or 1, n+m is 1 or 2, at least one of said R″ groups being an aliphatic hydrocarbon group containing from about 50 to about 500 carbon atoms, said phenolic group being bonded through a methylene group to a nitrogen atom of an amine, said amine containing from 1 to about 10 nitrogen atoms and from 1 to about 30 carbon atoms; wherein the molar ratio of A to B is from about 1:2 to about 6:1.

The first component of the combination dispersant of the present invention is the succinimide dispersant

having in its structure a hydrocarbon-substituted succinoyl group. The most preferred aliphatic hydrocarbon substituent is derived from an olefin polymer having a molecular weight of from about 700 to about 5,000. These include the olefin polymers mentioned above which have the more preferred molecular weight. Of the above, polybutene is most preferred. Optionally, a high molecular weight olefin polymer, for example, one having a molecular weight of 50,000 or more, can be degraded to produce an olefin polymer having a more preferred molecular weight. Methods of reducing the carbon chain length of olefin polymers by shearing are well known. Mere heating with mechanical stirring will reduce molecular weight. Air can be injected into a heated polymer to cause degradation and reduce molecular weight. Extrusion through an orifice under pressure causes chain scission. Any combination of such methods can be used.

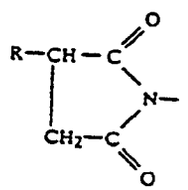
Highly preferred olefin polymers for use in making the succinic substituent are polymers of butene. Of these, the most preferred are the polybutenes having a number average molecular weight of from about 900 to about 2,100.

The hydrocarbon substituent can be introduced by heating a mixture containing the olefin polymer and maleic anhydride to a temperature of from about 200° to about 250°C. The reaction can be catalyzed by injecting chlorine. Likewise, a peroxide catalyst can be used. The reaction is preferably conducted in a mineral oil diluent which can remain in the succinic product to act as a solvent in later stages of the preparation. The aliphatic hydrocarbon-substituted succinic anhydrides are well known. The above-described hydrocarbon-substituted succinic compounds are then reacted with an amine. The preferred amines for use in making the succinic dispersants are the polyalkyleneamines. They are sometimes referred to as alkylene polyamines or polyalkylene polyamines. These amines consist mainly of polyamines having the structure

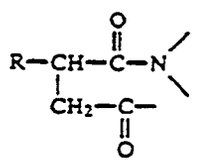
$$H_2N\{R'''\text{-}NH\}_p\text{-}H$$

wherein R''' is a divalent aliphatic hydrocarbon group containing 2 to about 4 carbon atoms and p is an integer from 1 to about 6. Representative examples are ethylenediamine. 1,2-propylenediamine, 1,2-butylenediamine, 1,3-propanediamine, diethylenetriamine, triethylene tetramine, tetraethylene pentamine (TEPA), pentaethylene hexamine, hexaethyleneheptamine and the like. Of these, the most preferred are the polyethylene amines containing from about 2 to about 6 ethylene amine units such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, and the like, including mixtures thereof which mixtures are most preferred. These preferred polyethylene amines are not oxyalkylated and therefore consist of from about 2 to about 6 ethylene amine units.

The aliphatic hydrocarbon-substituted succinic compound can be shown by the following structure:



in which the remaining bond on nitrogen is bonded to the remaining part of the polyamine. Amide formation can be illustrated by the structure:

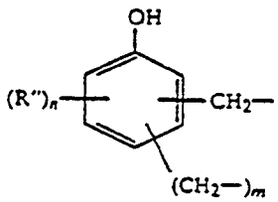


In practice, the product is a mixture of imides and amides with the majority of the product having succinimide units. In addition, the imides are a mixture of mono- succinimides and bis-succinimides depending on the molar proportion of the aliphatic hydrocarbon-substituted succinic compound to the polyamine. Preferably, this molar ratio is from about 1.5:1 to about 2.2:1, most preferably from about 1.6:1 to about 2.0:1. The most preferred molar ratio is about 1.8:1.

It is known in the art that the succinimide dispersants can be post-treated with, for example, a boron compound, a phosphorus compound, maleic anhydride, and combinations thereof. Such post-treated materials can also be utilized in the combination of the present invention. Methods for preparing succinimide dispersants and post-treated succinimides are well known and are disclosed, for example, in U.S. Patent Nos. 4,234,435;

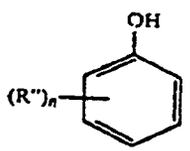
4,873,004; 3,172,892; 3,219,666; 4,686,054; and 3.950,341.

The second required component of the combination of the present invention is the Mannich dispersant made from an aliphatic hydrocarbon-substituted phenol, an aldehyde, or aldehyde precursor and an amine having at least one primary or secondary amine group. This leads to a Mannich condensate which can be defined by the presence within its structure of analiphatic hydrocarbon-substituted phenolic group having the formula



wherein R" is an aliphatic hydrocarbon group containing from one to about 500 carbon atoms, and n is one or two, m is 0 or 1 and n+m is 1 or 2. At least one R" group contains from about 50 to about 500 carbon atoms. The methylene bridge(s) is (are) bonded to a nitrogen atom of the amine. Such dispersants are well known and can be represented by the following U.S. Pat. Nos. 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,725,277; 3,539,633; 3,634,515; 3,697,574; 3,703,536; 3,704,308; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 4,142,980; 4,006,089; 3,980,569; 4,071,327; 4,070,402; 3,985,802; 4,161,475; 4,170,562; 4,016,092 and British Pat. No. 1,362,,013, incorporated herein by reference.

The Mannich dispersants are readily made starting with an aliphatic hydrocarbon-substituted phenol having the formula



wherein R" and n are as previously defined. These compounds can be made by reacting an olefin having the proper molecular weight with phenol or a monoalkyl substituted phenol. The olefin should contain from about 50 to about 500 carbon atoms which give a molecular weight of from about 700 to about 7,000. The olefin reactant is preferably made by polymerizing a lower olefin such as ethylene, propylene, isobutylene, hexene-1, octene-1 and mixtures thereof. Thus, useful olefin polymer reactants are polybutene, polypropylene, ethylene-propylene copolymer, and the like. Terpolymers can also be used to introduce the aliphatic hydrocarbon group. These include ethylene-propylene copolymers with dienes such as a 1,4-hexadiene, 1,5-hexadiene, 1,4-cyclooctadiene, dicyclopentadiene, and the like.

The more preferred aliphatic hydrocarbon-substituted phenol reactant is polybutenyl phenol made by reacting a polybutene of from 700 to about 7,000 molecular weight with phenol using a BF_3 catalyst such as BF_3 phenate or the like at 0°-60° C. Some more preferred reactants are those in which the polybutenyl group has a molecular weight of from about 1,000 to about 3, 000.

The methylene bridge attached at one end of the phenol is introduced by reaction with an aldehyde such as formaldehyde or a formaldehyde precursor such as paraformaldehyde. One or two of such bridges may form.

The other end of the methylene bridge is bonded to a nitrogen atom of an amine. Preferred amines contain from 1 to about 10 nitrogen atoms and from 1 to about 30 carbon atoms. More preferred amines are aliphatic amines. Examples of such amines are methyl amine, ethyl amine, isobutyl amine, lauryl amine, oleyl amine, stearyl amine, eicosamine, tricontamine, N-propylethylene diamine. N-dodecyl-1,3-propanediamine, N-(eicosylaminoethyl)ethylenediamine, N-aminoethylpiperazine, 1,3-propanediamine, N,N-dimethyl-1,3-propanediamine, 1,6-hexane diamine and the like.

A preferred class of amines for use in making the Mannich dispersants is the polyalkyleneamines which were also a preferred class of amines for use in making the succinimide dispersants. They were previously described and exemplified.

The Mannich dispersants are made by reacting about one mole of aliphatic hydrocarbon-substituted phenol with from about 0.9 to about 2.5 moles of formaldehyde or formaldehyde precursors, and from about 0.1 to about 2.0 moles of amine. These can be reacted in any order or altogether. In a preferred method, the Mannich dispersant is made by heating a mixture of aliphatic hydrocarbon substituted phenol and an amine at a temperature

of from about 60° to about 200°C and adding a formaldehyde to the heated mixture to form a Mannich condensate.

The subject Mannich dispersants may be post-treated with a boron compound such as, for example, boric acid. Useful boron compounds and methods for boronating the Mannich dispersants are well known in the art. See, for example, U.S. Patent Nos. 3,751,365 and 3,756,953. However, preferable Mannich dispersants are those which are non-boronated.

Each of the two types of additives is used in a lubricating oil composition at a concentration which maximizes their total effectiveness at an acceptable cost. A useful concentration range for each is from about 0.05 to about 10 weight percent. A more preferred range is from about 0.5 to about 5 weight percent and a most preferred range is from about 1 to about 4 weight percent. These concentrations do not include any mineral oil diluent incorporated into the additive during manufacture.

The molar ratio of the hydrocarbon-substituted succinimide to the Mannich dispersant is preferably from about 1:2 to about 6:1. More preferably, the molar ratio is from about 1:1 to about 4:1, and a most preferred ratio is 2:1.

Typically, the dispersant combination of the present invention is provided in the form of a concentrate comprising the dispersant combination and diluent oil. These concentrates can contain optional additives. For example, detergent additives are one such optional additive. As used in the compositions of the present invention, such detergent additives include alkali and alkaline earth metal petroleum sulfonates and salicylates, alkali and alkaline earth metal alkyl or alkaryl sulfonates, alkyl phenates and metal carboxylates. Examples of these are calcium petroleum sulfonates and salicylates, magnesium petroleum sulfonates and salicylates, barium alkaryl sulfonates and salicylates, magnesium petroleum sulfonates and salicylates, barium alkaryl sulfonates and salicylates, calcium alkaryl sulfonates and salicylates, magnesium alkaryl sulfonates and salicylates and calcium, and magnesium alkylsulfonates and salicylates. Both neutral and overbased sulfonates, salicylates or phenates, which have base number up to about 600 to provide acid neutralizing properties, can be beneficially used and are commercially available. These detergent additives are generally used in an amount to provide from about 0.05 to about 1.5 weight percent (based on the concentrate) alkaline earth metal and more preferably from about 0.1 to about 1.0 weight percent. The lubricating oil compositions of the present invention preferably contain a calcium petroleum sulfonate or an alkaryl (e.g., alkylbenzene) sulfonate as a detergent additive.

Additional optional additives for the compositions of the present invention include ashless antioxidants such as hindered alkyl phenols, alkyl diphenyl amines, and sulfur-bridged alkyl phenols; antiwear/corrosion inhibitors such as dialkyl selenides, metal dithiocarbamates, sulfurized terpenes and zinc dihydrocarbyldithiophosphates (ZDDP); friction reducers and extreme pressure (EP) additives such as N-alkylglycine-amides, chlorinated paraffins, sulfurized olefins, sulfurized fatty oils, sulfurized hydroxy substituted fatty amides, and co-sulfurized fatty acid amides and esters; antifoam agents such as acrylate copolymers and silicones; and surfactants such as ethoxylated alkyl phenols and poly(alkyleneoxides).

The above-described optional additives will be utilized in effective amounts (expressed below as weight percent based on the concentrate). For example, to the concentrates containing the dispersant combination of the present invention can be added up to about 10 weight percent ashless antioxidants (preferably about 0.05 to 5 weight percent), up to about 15 weight percent detergent (preferably about 5 to 10 weight percent), up to about 10 weight percent antiwear/corrosion inhibitor (preferably about 0.05 to 5 weight percent), up to about 10 weight percent friction reducer (preferably about 0.05 to to 5 weight percent), up to about 2 percent surfactant (preferably about 0.1 to 1 percent) and up to about 1 weight percent antifoam (preferably about 0.01 to 0.1 weight percent).

The concentrates of the present invention can be formed using conventional blending equipment and techniques. They are blended with base oils in amounts to provide the required additive levels in the finished crankcase lubricating oils, e.g., treat rates of from about 10 to about 20 percent by weight. Suitable base oils, as known in the art, include both mineral and synthetic oils and blends thereof.

Mineral oils include those of suitable viscosity refined from crude oil from all sources including Gulf Coast, Mid-Continent, Pennsylvania, California, Mideast, North Sea, Alaska, and the Far East and the like. Various standard refinery operations are useful in processing the mineral oil.

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymlers of alpha-olefins having the proper viscosity. Especially useful are the hydrotreated, liquid oligomers of C_6-C_{12} alpha-olefins such as alpha-decene trimer. Likewise, alkyl-benzenes of proper viscosity can be used as a synthetic oil, such as didodecyl benzene.

Useful synthetic esters include the esters of both monocarboxylic acids and polycarboxylic acids as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, trimethylol propane tripelargonate, pentaerythritol tetracaproate, di (2-ethylhexyl)adipate, dialauryl secacate and the like. Complex esters

prepared from mixtures of mono- and dicarboxylic acids and mono- and polyhydroxyl alkanols can also be used.

To illustrate the effectiveness of the combination dispersant of the present invention, two SAE 30 lubricating oil compositions were prepared. Blend A includes 6 weight percent of a commercial 1300 Mn polyisobutenyl succinimide dispersant available as HiTEC® 646 from Ethyl Petroleum Additives, Inc., St. Louis, MO. Blend B includes only 4 weight percent of the succinimide dispersant and was combined with 2 weight percent of a commercial boronated Mannich condensation product dispersant available as Amoco 9250 from Amoco Chemical Corporation, Chicago, IL. These blends were tested in a VE engine (on different dates and at different labs). Results are reported in Table 1.

TABLE 1

	BLEND A			BLEND B		
Hours	192	240	288	192	240	288
Sludge[1]						
Average			5.98			8.97
Rocker Arm	8.82	7.63	5.93	9.09	8.92	8.58
Valve Deck	9.24	8.86		9.12	9.12	
cam Cover	9.12	7.31		9.45	9.31	
Calc. 5 part	9.08	8.14		9.22	9.13	
Varnish[2]						
Average			7.88			7.14
Piston Skirt			6.70			6.69
Rocker Arm	N/A	N/A		8.13	7.68	
Cam Cover	N/A	N/A		8.71	8.70	
Calc. 5 part	N/A	N/A		7.51	7.37	
Wear						
Max, mils	6.6	10.2	14.2	0.4	0.3	0.7
Avg, mils	4.2	6.32	8.84	0.17	0.18	0.45
1E	N/A	N/A	6.3	0	0.3	0.3
1I	N/A	N/A	8.8	0.2	0.2	0.4
2E	N/A	N/A	8.7	0.3	0.1	0.4
2I	N/A	N/A	6.1	0	0.2	0.3
3E	N/A	N/A	11.6	0	0.1	0.3
3I	N/A	N/A	7/4	0.4	0.1	0.7
4E	N/A	N/A	14.2	0.2	0.2	0.5
4I	N/A	N/A	7.6	0.3	0.3	0.7

[1] Sludge ratings are such that a "10" is perfect and a 9.0 is a pass. The higher the number, the better dispersancy.

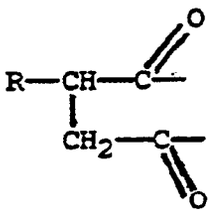
[2] For varnish ratings, a higher number indicates that less varnish is seen on a piston of the engine. A 10 is "perfect".

These results show that the combination of the present invention provides significantly reduced wear as well as significantly reduced low temperature sludge formation. It is contemplated that combinations having other succinimide type dispersants, e.g. boronated, and other Mannich type dispersants, e.g. non-boronated, will manifest similar results.

Claims

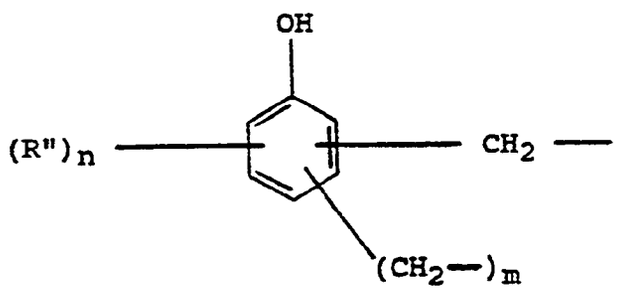
1. A composition suitable for use in a lubricating oil additive concentrate which composition comprises a combination of

(A) a succinimide dispersant having in its structure at least one hydrocarbon-substituted succinoyl group represented by the formula:



wherein R is an aliphatic hydrocarbon group having a number average molecular weight of from about 700 to about 5,000, said succinoyl group being bonded to a nitrogen atom of a polyalkyleneamine consisting of from about 2 to about 6 ethyleneamine units to form an amide and/or imide, the molar ratio of said succinoyl group to said polyethyleneamine being within the range of from about 1.5:1 to about 2.2:1; and

(B) a Mannich dispersant having in its structure a polybutene-substituted phenolic group represented by the formula:



wherein R″ is a polybutene group and n is 1 or 2, m is 0 or 1, n + m is 1 or 2, said R″ groups containing from about 50 to about 500 carbon atoms, said phenolic group being bonded through a methylene group to a nitrogen atom of an amine, said amine containing from 1 to about 10 nitrogen atoms and from 1 to about 30 carbon atoms;

wherein the molar ratio of A to B is from about 1:2 to about 6:1.

2. The composition of claim 1 wherein the R is polybutene having a number average molecular weight of from about 700 to about 5,000.

3. The composition of claim 1 or 2 wherein the polyethyleneamine is a mixture of polyethyleneamines consisting of from about 2 to about 6 ethyleneamine units.

4. The composition of any one of claims 1 to 3 wherein the molar ratio of the succinoyl group to the polyethyleneamine is from about 1.6:1 to about 2.0:1.

5. The composition of any one of the preceding claims wherein the molar ratio of A to B is from about 1:1 to about 4:1.

6. The composition of any one of the preceding claims wherein the Mannich dispersnat is boronated.

7. The composition of any one of the preceding claims wherein the succinimide dispersant is post-treated with a post-treating agent selected from the group consisting of a boron compound, a phosphorus compound, maleic anhydride and combinations thereof.

8. A lubricating oil additive concentrate comprising a composition of any one of the preceding claims.

9. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor dispersant amount of a composition of any one of claims 1 to 7 or concentrate of claim 8.

10. The use of a composition as defined in any one of claims 1 to 7 or concentrate as defined in claim 8, to reduce or prevent sludge formation in a lubricating oil.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3538

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-61 346 (EDWIN COOPER) September 29, 1982 * page 2, line 10 - page 4, line 15 * * page 5, line 6 - line 17 * * page 9, line 12 - line 15 * * page 11; example 1 * * page 13; example 4 * * claim 16 *	1-10	C10M163/00
D	& US-A-4 426 305 (R.E MALEC)		
Y	GB-A-1 000 883 (ESSO RES. ENG. COMP.) August 11, 1965 * page 1, line 33 - line 43 * * page 2, line 32 - line 33 * * page 3, line 43 - page 4, line 15 * * page 4, line 27 - line 36 *	1-10	
A	FR-A-2 354 380 (CHEVRON RES. COMP.) January 6, 1978 * page 4, line 19 - page 5, line 12 * * page 6, line 24 - line 33 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 AUGUST 1991	HILGENGA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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