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This invention relates to lubricating oil compositions exhibiting improved dispersancy in diesel engines. More particularly, the invention relates to a method of improving borated alkenyl succinimide dispersants through use of oil-soluble organic acids.

7 It is widely recognised that lubricating oils for
8 diesel engines are typically subjected to severe engine op-
9 erating conditions and that providing a highly potent sludge
10 dispersant is an important objective in the industry for
11 diesel engine lubricating oil formulations.

Dispersants based upon the borated derivatives of the reaction product of various polyamines with alkenyl hydrocarbon substituted succinic anhydrides or acids are known in the art and are disclosed with the unborated precursors, for example, in U.S. Patent 3,172,892, issued March 9, 1965 to LeSuer et al and U.S. Patent 3,933,659, issued January 20, 1976 to Lyle et al. The alkenyl portion of these dispersants is typically a polymer of a C₂-C₅ monoolefin, especially polyisobutylene.

The present invention provides enhancement of the dispersant potency of these borated alkenyl succinimide dispersants in diesel engines through use of very minor amount of certain organic acids.

25 In accordance with the present invention, there
26 is provided a lubricating oil composition exhibiting
27 improved dispersancy in a diesel engine comprising a hydro-
28 carbon lubricating oil and an acid-treated, oil-soluble
29 borated alkenyl succinimide dispersant, said dispersant
30 being acid-treated after boration by having incorporated
31 therein, per mole of said succinimide, 0.1 to 0.5 mole of
32 an oil-soluble organic acid having a pK of -10 to +5
33 containing a C₉-C₇₀ hydrocarbyl group.

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- 1 Oil-soluble alkenyl succinimide ashless dispersants are
- 2 those formed by reacting a polyalkenyl succinic acid or
- 3 anhydride with a polyalkyleneamine. The alkenyl

1 group of the succinic acid or anhydride is derived from a
2 polymer of a C₂ to C₅ monoolefin, especially a polyisobutyl-
3 ene wherein the polyisobutenyl group has a number average
4 molecular weight ($\bar{M}_n$) of about 700 to about 5,000, more
5 preferably about 900 to 1,500. While homopolymers of ethyl-
6 ene, propylene, butylene, isobutylene and pentene are pre-
7 ferred, copolymers of these mono-olefins are also suitable
8 for providing the polyalkenyl succinic acid or anhydride.
9 Preferred are the polyisobutenyl succinic anhydrides within
10 the aforesaid molecular weight range.

11 Suitable polyamines for reaction with the afore-
12 said succinic acid or anhydrides to provide the succinimide
13 are those polyalkyleneamines represented by the formula
14 $\text{NH}_2(\text{CH}_2)_n-(\text{NH}(\text{CH}_2)_m)_m-\text{NH}_2$ wherein n is 2 to 3 and m is 0 to
15 10. Illustrative are ethylene diamine, diethylene triamine,
16 triethylene tetramine, tetraethylene pentamine, which is
17 preferred, tetrapropylene pentamine, pentaethylene hexamine
18 and the like, as well as the commercially available mixtures
19 of such polyamines. These amines are reacted with the al-
20 kenyl succinic acid or anhydride in ratios of about 1:1 to
21 10:1 moles of alkenyl succinic acid or anhydride to poly-
22 amine, and preferably in a ratio of about 2:1.

23 The borated alkenyl succinimide dispersants are
24 also well known in the art as disclosed in U.S. Patent
25 3,254,025. These derivatives are provided by treating the
26 alkenyl succinimide with a boron compound selected from the
27 group consisting of boron oxides, boron halides, boron acids
28 and esters thereof, in an amount to provide from about 0.1
29 atomic proportion of boron to about 10 atomic proportions
30 of boron for each atomic proportion of nitrogen in the dis-
31 persant. The borated product will generally contain about
32 0.1 to 2.0, preferably 0.2 to 0.8, weight percent boron
33 based upon the total weight of the borated dispersant. Boron
34 is considered to be present as dehydrated boric acid poly-
35 mers attaching as the metaborate salt of the imide. The
36 boration reaction is readily carried out adding from about
37 1 to 3 weight percent based on the weight of dispersant,

1 of said boron compound, preferably boric acid, to the dis-
2 persant as a slurry in mineral oil and heating with stir-
3 ring from about 135° to 165°C for about 1 to 5 hours fol-
4 lowed by nitrogen stripping and filtration of the product.

5 Such borated derivatives of alkenyl succinimide
6 ashless dispersants are used customarily in lubricating oil
7 compositions in amounts ranging from 0.1 to 10 per cent,
8 preferably 0.5 to 5 per cent by weight based upon the total
9 weight of the finished compositions. The same amounts are
10 applicable to the acid-treated diesel oil dispersants of
11 the present invention.

12 The improved borated alkenyl succinimide disper-
13 sants used in the present invention are prepared by adding
14 a suitable acid to a solution of dispersant in hydrocarbon
15 lubricating oil base stock, preferably a concentrated
16 solution of about 40 to 60 wt.% dispersant, preferably
17 about 50 wt.%, is used. The same lubricating oil base
18 stock used in formulating the finished oil is a convenient
19 vehicle for providing the solution. Preferred base stocks
20 are paraffin mineral oils having a viscosity of about 20
21 to 100 cS min. (100°F) and blends of such oils. The acid
22 treatment is effected by heating the solution of dispersant
23 to about 80 to 200°C, preferably to about 100 to 175°C,
24 such as 150°C, and adding thereto 0.1 to 0.5 mole of a
25 suitable organic acid per mole of dispersant. The prefer-
26 able range of addition is about 0.2 to 0.3 mole per mole of
27 borated polyalkenyl succinimide dispersant. The mixture is
28 stirred at this temperature for about 15 minutes to 3 hours
29 until the acid reacts into the system. While not wishing
30 to be bound by this theory, it is believed that at this
31 relatively elevated temperature, a capping reaction occurs
32 whereby an amide is formed between unreacted amino
33 moieties and the organic acid additive. A convenient
34 method of conducting this acid treatment is to add the
35 organic acid as the final step in the dispersant
36 preparation process, i.e., after boration.

1 Subsequent to this, conventional lubricating oil blending
2 techniques are followed to provide finished lube oils
3 exhibiting improved dispersancy in diesel engines.

4 The oil-soluble organic acids which can be used
5 in accordance with this invention may be generally classi-
6 fied as those acids containing a hydrogen dissociating
7 moiety which has a pK of -10 to about + 5.0. The term pK
8 can be defined as the negative logarithm to the base 10 of
9 the equilibrium constant for the dissociation of the oil-
10 soluble organic acid.

11 As used herein, oil-soluble is defined as those
12 organic acids which themselves are substantially soluble in
13 mineral oil at 20°C to at least 50 weight percent.

14 Representative classes of the strong organic acids
15 containing oil-solubilizing groups suitable for reaction
16 with the borated dispersant are the hydrocarbyl substituted
17 maleic acids, malonic acids, phosphoric acids, thio-
18 phosphoric acids, phosphonic acids, thiophosphonic acids,
19 phosphinic acids, thiophosphinic acids, sulfonic acid,
20 sulfuric acid and alpha-substituted or nitrilocarboxylic
21 acids wherein the oil-solubilizing group or groups are
22 hydrocarbyl and containing from 9 to 70, preferably from 20
23 to 40, optimally 25 to 35, total carbon atoms. These
24 ranges are considered to approximate oil-solubility for the
25 general classes of organic acids suitable herein.

26 A preferred category of organic acids for use
27 with borated dispersants are the oil-soluble sulfonic acids
28 which are typically alkaryl sulfonic acids. These sulfonic
29 acids are typically obtained by the sulfonation of alkyl
30 substituted aromatic hydrocarbons such as those obtained
31 from the fractionation of petroleum by distillation and/
32 or extraction or by the alkylation of aromatic hydrocarbons
33 as, for example, those obtained by alkylating benzene,
34 toluene, xylene, naphthalene, diphenyl and halogen
35 derivatives such as chlorobenzene, chlorotoluene and
36 chloronaphthalene. The alkylation may be carried out
37 using known processes in the presence of a catalyst such as
38 $AlCl_3$ or BF_3 with alkylating

1 agents having from 9 to about 70 carbon atoms, such as
2 halo-paraffins, olefins that may be obtained by dehydro-
3 genation of paraffins, polyolefins from ethylene,
4 propylene, etc. Preferred sulfonic acids are those
5 obtained by the sulfonation of hydrocarbons prepared by
6 the alkylation of benzene or toluene with tri-, tetra-
7 or pentapropylene fractions obtained by the polymerization
8 of propylene. The alkaryl sulfonic acids contain from
9 9 to 70, preferably from 18 to 34, optimally from 22 to
10 30, carbon atoms per alkyl substituent on the aryl
11 group and these groups may be mono-alkylated or poly-
12 alkylated aryl moieties.

13 Particularly preferred is an alkylated benzene
14 sulfonic acid having a molecular weight ($\bar{M}_n$) of
15 from 475 to 600 wherein the alkyl substituent groups
16 contain about 18 to 34 carbons.

17 The oil-soluble phosphorous-containing acids
18 are a second preferred category of acids for reaction
19 with borated dispersants can be described as hydrocarbyl
20 substituted derivatives of phosphoric acid, R_3PO_4 ,
21 phosphonic acid $HP(O)(OH)_2$ or phosphinic acid $H_2P(O)(OH)$
22 which have at least one free acidic hydrogen and one or
23 two hydrogens are replaced by one or two C_9-C_{70}
24 hydrocarbyl radicals such as alkyl, aryl, alkaryl,
25 aralkyl and alicyclic hydrocarbon radicals to provide
26 the required oil solubility. C_9 to C_{30} mono- or
27 di-alkyl (mono- or di-acid phosphates) derivatives of a
28 H_3PO_4 are a particularly preferred sub-category of
29 acids for use in improving diesel dispersancy and
30 tridecyl mono/dihydrogen phosphonic acid is a preferred
31 embodiment. Suitable acids include also the corresponding
32 C_9-C_{70} hydrocarbyl mono or di-substituted thiophosphoric,
33 thiophosphinic or thiophosphonic acids.

34 The acids are usually prepared by reacting P_2O_5
35 or P_2S_5 with the desired alcohol or thiol to obtain the
36 substituted phosphoric acids.

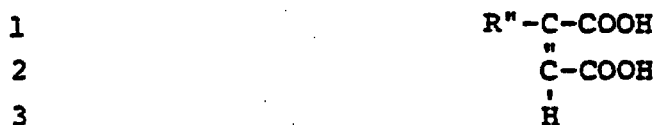
37 The desired hydroxy or thiol compound should contain
38 hydrocarbyl groups of from about 9 to about 70 carbon
39 atoms with preferably about 15 total carbon atoms average

1 to provide oil solubility to the product. Examples of
2 suitable compounds are nonyl alcohol, dodecyl alcohol,
3 stearyl alcohol, amylphenol, octylphenol, nonylphenol,
4 alkylated naphthol, etc., and their corresponding thio
5 analogues; and mixtures of alcohols and/or phenols such as
6 isobutyl alcohol and nonyl alcohol; orthocresol and nonyl-
7 phenol; etc., and mixtures of their corresponding thio
8 analogues.

9 In the preparation of the hydrocarbyl-substituted
10 thiophosphoric acids, any conventional method can be used,
11 such as the preparations described in U.S. Patents
12 2,552,570, 2,579,038 and 2,689,220. By way of illustration,
13 a dialkaryl-substituted dithiophosphoric acid is prepared by
14 the reaction of about 2 moles of P_2S_5 with about 8 moles of
15 a selected alkylated phenol, e.g., a mixture of C_8 - C_{12} alkyl-
16 substituted phenols, i.e., nonyl phenol, at a temperature
17 of from $50^\circ C$ to $125^\circ C$ for about 4 hours. In the preparation
18 of hydrocarbyl substituted thiophosphinic acids, as con-
19 ventionally known, a disubstituted phosphine is oxidized to
20 give disubstituted thiophosphinic acids (see F.C. Whitmore's
21 "Organic Chemistry", published by Dover Publications, New
22 York, NY (1961), page 848).

23 Particularly preferred for preparation of oil-
24 soluble phosphoric, phosphonic and phosphinic acids useful
25 in the process of the invention are mixed aliphatic alcohols
26 obtained by the reaction of olefins with carbon monoxide
27 and hydrogen and subsequent hydrogenation of the resultant
28 aldehydes to form the "Oxo" alcohols, which will contain
29 an average of about 13 carbon atoms, such as a di- C_{13} Oxo
30 phosphoric acid. The oil-soluble phosphorous-containing
31 acids are readily prepared from these alcohols by reaction
32 with P_2O_5 , as is well known in the art.

33 Another class of useful strong organic acids are
34 oil-soluble hydrocarbyl-substituted maleic acids of the
35 general formula:



wherein R'' is an oil-solubilizing, hydrocarbyl group containing from about 9 to 70 carbons. Representative of these oil-soluble maleic acid derivatives are pentadecylmaleic acid, hexadecylmaleic acid, eicosylmaleic acid, triacontanyl-maleic acid and polymers of C₂-C₅ monoolefins having from 15 to 70 or more carbons substituted onto said maleic acid.

Additional suitable strong acids are those oil-soluble C₉-C₇₀ hydrocarbyl-containing substituted malonic acids of the general formula:



wherein R'' has the meaning set forth above as an oil-solubilizing hydrocarbyl group which is illustrated by the following representative compounds which include the malonic acid counterparts of the above-referenced hydrocarbyl substituted maleic acids, i.e., pentadecylmalonic acid, hexadecyl malonic acid, etc.

Another class of useful acids are oil-soluble C₉-C₇₀ hydrocarbyl-substituted sulfuric acids of the general formula R''HSO₄ wherein R'' is the hydrocarbyl oil-solubilizing group as exemplified by pentadecylsulfuric acid, hexadecylsulfuric acid, eicosylsulfuric acid, triacontanylsulfuric acid, etc.

A further group of acids which can be used in accordance with this invention are oil-soluble mono- and di-alpha-substituted hydrocarbyl carboxylic acids having the general formula:



wherein R'' is a C₉-C₇₀ hydrocarbyl, oil-solubilizing group as referenced above and X refers to hydrogen, nitrilo, nitro, halo, such as chloro, or a cyano group or groups. These materials are represented by the following: alpha-nitro

1 and alpha-di-nitro substituted acids, such as dodecanoic,
2 pentadecanoic, octadecanoic, docosanoic, octacosanoic, tri-
3 contanoic, tetracontanoic and the like.

4 The invention is further illustrated by the
5 following example:

6 EXAMPLE

7 A paraffinic mineral oil solution was prepared
8 containing 49 wt. % of a polyisobutenyl succinic anhy-
9 dride/polyamine dispersant ($\bar{M}_n=980$; 2.2 moles of succinic
10 anhydride per mole of polyamine). The polyamine was a
11 mixture of alkylene polyamines approximating tetraethylene
12 pentamine available under the trade name "DOW E-100" from
13 Dow Chemical Co., Midland, Michigan. This dispersant has
14 been borated by reaction with a slurry of 1.4 moles of
15 boric acid in mineral oil and the final product contained
16 1.5 wt. % nitrogen and 0.5 wt. % boron.

17 Three acid-treated dispersant materials in accor-
18 dance with this invention were provided by:

19 (1) Incorporating into a 50 wt. % solution of
20 dispersant in the mineral oil 1.2 wt. % of tridecyl mixed
21 mono and di-acid phosphate by adding in the phosphate and
22 stirring the mixture at about 150°C for 30 minutes.

23 (2) Incorporating into the dispersant solution
24 2.5 wt. % (0.2 molar equivalents) of an alkyl benzene sul-
25 fonic acid having an $\bar{M}_n=530$ by adding the acid to a 50
26 wt. % solution of dispersant in the mineral oil at 150°C.

27 (3) Incorporating into the dispersant solution
28 1.0 wt. % (0.08 molar equivalents) of the same sulfonic
29 acid as in subparagraph 2 above using the same blending
30 technique.

31 Lubricating oil formulations were prepared con-
32 taining the standard borated dispersant before acid modifi-
33 cation, noted below as Base Formulation and formulations
34 containing each of the three acid-modified borated disper-
35 sants, and noted corresponding below as Formulations 1, 2,
36 and 3. Each formulation was an SAE 10W30 quality crankcase
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1 oil which also contained conventional amounts of an olefin
2 copolymer V.I. improver, a rust inhibitor, a metal deter-
3 gent and a zinc dialkyldithiophosphate in a mineral oil
4 base. These formulated oils were each subjected to engine
5 testing in the "Caterpillar 1H-2" test which is an in-
6 dustry and government accepted test for the dispersancy
7 and overall effectiveness of diesel oil lubricants. The
8 results and explanation of the test are given below:

9	240 Hour Caterpillar 1H-2 Test	
	TGF ²	WTD ³
10 <u>Formulation</u>		
11 Base ¹	16.6%	189.1
12 No. 1	0.5%	55.2
13 No. 2	6.0%	37.0
14 No. 3	1.0%	106

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16 ¹Base - this result is an average data base used for com-
17 parison in evaluating new diesel formulations and
18 is an average of 25 engine tests.

19 ²TGF - top groove fill, % deposits in groove

20 ³WTD - weighted total demerits

21 The Caterpillar 1H-2 test is also a U.S. Federal
22 Test Method 791-346 and is used to meet military specifica-
23 tions, such as MIL-L-21260B and industry specifications,
24 such as SAE 183 and General Motors GM 6146M. The purpose
25 of the test is to determine the effect of an oil on ring
26 sticking, wear and accumulation of deposits. The test uses
27 a single cylinder Caterpillar diesel 5 1/8" x 6 1/2".

28 For the 1H-2 test WTD (Weighted Total Demerits)
29 is the principal value and for a 240 hour test, the target
30 specification is a value below the 75-80 range. This is
31 derived from the published specification target of WTD 140
32 for a 480 hour test. WTD is a cumulative rating based on
33 observation of deposits in the groove and land areas of the
34 piston and lacquer on piston skirts with all these specific
35 evaluations being weighted according to their relative im-
36 portance and the final WTD value being calculated in accor-
37 dance with the test procedure.



CLAIMS

1. A lubricating oil composition exhibiting improved dispersancy in a diesel engine comprising a hydrocarbon lubricating oil and an acid-treated, oil-soluble borated alkenyl succinimide dispersant, said dispersant being acid-treated after boration by having incorporated therein, per mole of said succinimide, 0.1 to 0.5 mole of an oil-soluble organic acid having a pK of -10 to +5 containing a C₉-C₇₀ hydrocarbyl group.
 2. The composition of claim 1 wherein the organic acid is an alkaryl sulfonic acid.
 3. The composition of claim 2 wherein the sulfonic acid is a C₉-C₇₀ alkyl-substituted benzene sulfonic acid.
 4. The composition of claims 1-3 wherein the acid treatment is with about 0.2 to 0.3 mole of said acid.
 5. The composition of claims 1-4 wherein the acid is an alkylated benzene sulfonic acid having an Mn of from about 475 to 600.
 6. The composition of claim 1 wherein the acid is an oil-soluble phosphorous-containing acid.
 7. The composition of claim 6 wherein the acid is a C₉-C₇₀ hydrocarbyl-substituted phosphoric acid.
 8. The composition of claim 7 wherein the acid is a C₉-C₃₀ mono- or di- alkyl acid phosphate.
 9. The composition of claim 7 wherein the acid is tridecyl mono/dihydrogen phosphoric acid.
 10. The composition of claim 9 wherein the acid treatment is with 0.2 to 0.3 mole of acid per mole of said succinimide dispersant.
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