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3,745,117

LUBRICATING OIL COMPOSITION

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U.S. Cl. 252—48.2

5 Claims

ABSTRACT OF THE DISCLOSURE

A high efficiency, lubricating oil composition comprises (a) a large amount of lubricating oil, (b) a 4,4'-thiobis phenol, and (c) a substituted phenol having at least one tertiary butyl group in the ortho position to the hydroxyl group. Said lubricating oil composition is, for example, a high efficiency turbine oil.

FIELD OF THE INVENTION

This invention relates to a high efficiency lubricating oil composition and also to a process for preparing the lubricating oil composition, belonging to a mineral oil that exhibits surpassing efficiency, from a feedstock oil being devoid particularly of oxidation stability and effect of using additives.

BACKGROUND OF THE INVENTION

As regards a high efficiency lubricating oil composition, for instance, turbine oil, the use of a highly refined feedstock oil as a base oil or the use of a special composition also as a base oil has been disclosed. However, in order to prepare such a base oil, it is required to rely on a special crude oil. Further, the preparation of said base oil according to a conventional processing step is practically infeasible because of economical reasons. Still further, said special composition is least recommendable, since it is seldom available to those in the art.

SUMMARY OF THE INVENTION

The inventors of the present invention have successfully overcome a series of such difficulties. It is therefore the primary object of the present invention to provide turbine oil, exhibiting surpassing efficiency comparable to a lubricating oil composition which makes use of a highly refined base oil, from crude oil.

It is another object of the present invention to provide a highly efficient turbine oil by use of an easily available base oil which is obtainable without particularly enhancing any refining quality thereof through a special combination of a thiobisphenol and a substituted phenol which have already proved effective as an antioxidant.

In further object, according to a process for preparing a lubricating oil by a hydrogen refining process which has given tendency to frequent adoption during the recent years, it is possible to obtain a lubricating base oil, having a property resembling that of a highly refined oil, from a conventional special crude oil. The property of the thus obtained lubricating base oil is however found to be inferior to the property in respect of stability, particularly in respect of anti-corrosive property because of

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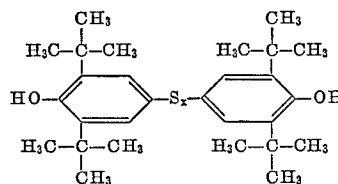
copresence of aromatic components such as sulfur- or nitrogen-containing heterocyclic compounds involved therein.

The present invention is, on the other hand, capable of substantially eliminating these defects.

DETAILED DESCRIPTION OF THE INVENTION

In the following will be given a further embodiment of this invention, in greater detail. That is to say, the present invention covers a highly efficient lubricating oil composition belonging to a mineral oil through the combined use of (a) 4,4'-mono-, di- or tri-thiobis (2,6-di-t-butylphenol), (b) other additives, and (c) a base oil having reduced oxidation stability and poor effect from additives.

4,4'-mono-, di- or tri-thiobis (2,6-di-t-butylphenol) to be used in the present invention are the compounds represented by the following general formula



(wherein x represents an integer of from 1 to 3).

In order to obtain a lubricating oil composition of the present invention, it is required to use said 4,4'-thiobis (2,6-di-t-butylphenol)s in combination with additives.

Compounds to be included in the additives in said (b) are a substituted phenol having 1 or 2 tertiary butyl groups in the ortho position to the hydroxyl group thereof, for example, 2,6-di-t-butyl-p-cresol, 2,6-di-t-butyl-4-ethylphenol, 4,4'-methylenebis (2-t-butyl-5-methylphenol) and also 4,4'-bis (2-t-butyl-5-methylphenol) and the like.

The combined use of the aforementioned thiobisphenols and substituted phenols assures successful providing of a lubricating oil composition, having a favorable oxidation stability, from a base oil abundant in sulfur content. It also provides a lubricating oil composition, having surpassing property, from a high pressure hydrogen refined oil having less aromatic content. Furthermore, it is naturally a matter of course that other additives of conventional use, such as an antifoamer and a rust preventive or the like can also be used in combination with lubricating oil composition of this invention.

The amount of a thiobisphenol and the substituted phenols to be used in the present invention may vary depending on the diversified uses of the lubricating oil. The ratio of said thiobisphenols to the substituted phenols in amount may also vary accordingly. Generally, a thiobisphenol is used in an amount of less than 5% by weight based on the weight of total composition, preferably in a range of from 0.01 to 0.1% by weight, while substituted phenols in an amount of less than 5% by weight, preferably in a range of from 0.1 to 0.5% by weight, respectively. In other words, from about 1 to about 50 parts by weight of the substituted phenol is used for each part by weight of the thiobis phenol.

According to the present invention, the use can be made of any one of various lubricating base oils having the sulfur content of approximately 5% by weight or below.

Hereinunder will be given further embodiments the present invention in greater detail by way of examples. It should be noted however that this invention will in no way be limitative, but will merely illustrate some of the essential feature thereof. All percentages shown in following examples are based on the weight of the total composition, unless otherwise specified.

EXAMPLES 1-20

By using a solvent refined lubricating base oil, a commercially available rust preventive, an antifoamer, 0.50% of 2,6-di-tertiary butyl paracresol and thiobisphenols illustrated in Table 1, 20 turbine oil blends were prepared. Thereafter, an oxidation stability test was conducted as to each one of these turbine oils on the basis of ASTM D943. The results are shown in Table 1 to follow.

TABLE 1.—TURBINE OIL OXIDATION STABILITY TEST RESULTS ON THE BASIS OF ASTM D943

Ex. No.	Composition	Time required for the total acid value to reach 1.0 mg. KOH/g. (hr.)
1*	Base oil A ¹	1,120
2*	Base oil A and 0.01% of organic zinc dithiophosphate.....	1,310
3.....	Base oil A and 0.05% S ²	3,040
4.....	Base oil A and 0.05% SS ³	3,690
5*	Base oil A and 0.01% of 4,4'-thiobis (6-t-butyl-p-cresol).....	1,260
6.....	Base oil A and 0.01% S ²	2,820
7.....	Base oil A and 0.01% SS ⁴	2,860
8.....	Composition in Example 2 and 0.01% S ²	2,800
9.....	Composition in Example 2 and 0.01% SS ⁴	2,910
10.....	Composition in Example 2 and 0.05% S ²	3,170
11*	Base oil B ¹	1,220
12.....	Base oil B and 0.01% of organic zinc dithiophosphate.....	1,340
13.....	Base oil B and 0.01 S ²	2,750
14.....	Base oil B and 0.05% S ²	3,070
15.....	Base oil B and 0.01% SS ⁴	2,860
16.....	Base oil B and 0.05% SS ⁴	3,570
17.....	Composition in Example 12 and 0.01% S ²	2,720
18.....	Composition in Example 12 and 0.05% S ²	2,980
19.....	Composition in Example 12 and 0.01% SS ⁴	2,690
20.....	Composition in Example 12 and 0.05% SS ⁴	3,110

¹ The lubricating base oil contains 0.50% of 2,6-di-tertiary butyl paracresol. This base oil used is from the Middle East and is solvent refined. It contains 0.52% of sulfur and has 31.50 centistokes of kinematic viscosity at 37.8° C. and 5.18 centistokes of kinematic viscosity at 98.9° C., respectively.

² The lubricating base oil contains 0.50% of 2,6-di-tertiary butyl paracresol. This base oil used is from the Middle East and is solvent refined. It contains 0.32% of sulfur and has 30.30 centistokes of kinematic viscosity at 37.8° C. and 5.09 centistokes of kinematic viscosity at 98.9° C., respectively.

³ 4,4'-thiobis (2,6-di-t-butylphenol).

⁴ 4,4'-dithiobis (2,6-di-t-butylphenol).

* Reference example.

Examples 21-40

By using a high pressure hydrogen refined lubricating base oil, a rust preventive (Lubrizol 859), 0.50% of 2,6-di-t-butyl-p-cresol and thiobisphenols illustrated in Table 2, 20 (turbine oil) compositions were prepared.

An oxidation stability test of a turbine oil was conducted on the basis of ASTM D943. The results are shown in Table 2 to follow.

TABLE 2.—TURBINE OIL OXIDATION STABILITY TEST RESULTS ON THE BASIS OF ASTM D943

Ex. No.	Composition	Time required for the total acid value to reach 1.0 mg. KOH/g. (hr.)
21*	Base oil C ¹	450
22*	Base oil C and 0.01% of organic zinc dithiophosphate.....	2,260
23.....	Base oil C and 0.01% S ²	3,120
24.....	Base oil C and 0.01% SS ⁴	3,450
25.....	Base oil C and 0.05% S ²	3,240
26.....	Base oil C and 0.05% SS ⁴	3,480
27.....	Composition in Example 22 and 0.01% S ²	2,890
28.....	Composition in Example 22 and 0.01% SS ⁴	3,010
29.....	Composition in Example 22 and 0.05% S ²	3,060
30.....	Composition in Example 22 and 0.05% SS ⁴	3,180
31*	Base oil D ²	800
32*	Base oil D and 0.01% of organic zinc dithiophosphate.....	1,100
33*	Base oil D and 0.02% of Suntorene C (trade name).....	1,570
34*	Base oil D and 0.05% of pyrrolidone.....	1,400
35.....	Base oil D and 0.01% S ²	3,310
36.....	Base oil D and 0.01% SS ⁴	3,350
37.....	Composition in Example 32 and 0.01% S ²	3,120
38.....	Composition in Example 32 and 0.01% SS ⁴	3,250
39.....	Composition in Example 32 and 0.05% S ²	3,330
40.....	Composition in Example 32 and 0.05% SS ⁴	3,490

¹ Contains 2% of aromatic hydrocarbon by silica gel chromatographic analysis. It also allowed to contain 2,6-di-t-butyl para-cresol of a 0.05% high pressure hydrogen refined lubricating base oil having 28 centistokes of kinematic viscosity at 37.8° C. and 4.98 centistokes of kinematic viscosity at 98.9° C.

² Contains 12% of aromatic hydrocarbon through silica gel chromatographic analysis. It also contains 2,6-di-t-butyl para-cresol a 0.50% high pressure hydrogen refined lubricating base oil having 33 centistokes of kinematic viscosity at 37.8° C. and 5.37 centistokes of kinematic viscosity at 98.9° C.

Footnotes 3 and 4—Same as in Table 1.

* Reference example.

Examples 41-53

By using a solvent refined lubricating base oil from the Middle East crude oil containing, as a base oil, 0.52% of sulfur, and exhibiting a kinematic viscosity of 1.50 centistokes at 37.8° C. and 5.18 centistokes at 98.9° C., a rust preventive (Lubrizol 859) and also using various additives illustrated in Table 3, a catalytic oxidation test was conducted. The adding ratio of the additives and the testing results are as per illustrated in Table 3 to follow.

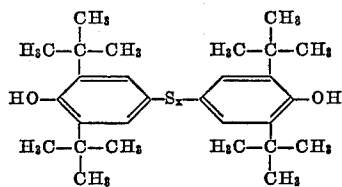
TABLE 3.—CATALYTIC OXIDATION TEST AT 120° C.

Example number	Additive (adding ratio, weight, percent)	Oxidation life, hr.	Total acid value, mg. KOH/g.	Formation of sludge
41 (Reference example).....	2, 6-di-t-butyl-p-cresol (0.25).....	360	2.4	Yes.
42 (Reference example).....	2, 6-di-t-butyl-p-cresol (0.25).....	360	1.8	Yes.
43 (Reference example).....	2, 2'-methylenbis (6-butyl-4-methylphenol) (0.25).....	200	1.0	Yes.
44 (Reference example).....	2, 2'-methylenbis (6-butyl-4-methylphenol) (0.25).....	200	1.0	Yes.
45 (Reference example).....	4, 4'-thiobis (6-t-butyl-3-methylphenol) (0.03).....	200	2.0	Yes.
46 (Reference example).....	4, 4'-thiobis (2,6-di-t-butylphenol) (0.1).....	360	2.6	Yes.
47 (Reference example).....	4, 4'-thiobis (2,6-di-t-butylphenol) (0.1).....	360	1.2	No.
48 (Reference example).....	4, 4'-thiobis (2,6-di-t-butylphenol) (0.1).....	360	2.1	No.
49 (Reference example).....	4, 4'-dithiobis (2,6-di-t-butylphenol) (0.2).....	300	1.0	No.
50 (Reference example).....	(2, 6-di-t-butyl-p-cresol (0.5).....	360	1.6	No.
51 (Reference example).....	(4, 4'-thiobis (6-t-butyl-3-methylphenol) (0.03).....	500	1.0	No.
52 (Reference example).....	(2, 6-di-t-butyl-p-cresol (0.5).....	500	0.84	No.
53 (Reference example).....	(4, 4'-thiobis (2,6-di-t-butylphenol) (0.01).....	500	0.65	No.

We claim:

1. A lubricating oil composition, characterized by comprising

- (a) a major amount of lubricating base oil;
 (b) from about 0.01 to 0.1 weight percent of a 4,4'-thiobis phenol represented by the general formula



- (wherein x represents an integer of from 1 to 3); and
 (c) from about 0.1 to about 0.5 weight percent of a substituted phenol selected from the group consisting of 2,6-di-*t*-butyl-*p*-cresol, 2,6-di-*t*-butyl-4-ethylphenol, 4,4'-methylenebis (2-*t*-butyl - 5 - methylphenol) and 4,4'-bis (2-*t*-butyl-5-methylphenol).

2. A lubricating oil composition according to claim 1, in which said thiobis phenol is 4,4'-thiobis (2,6-di-*t*-butylphenol).

3. A lubricating oil composition according to claim 1,

in which said thiobis phenol is 4,4'-thiobis (2,6-di-*t*-butylphenol).

4. A composition of matter comprising a 4,4'-thiobis phenol as defined in claim 1 and a substituted phenol as defined in claim 1.

5. A composition of matter comprising from about 1 to about 50 parts by weight of a substituted phenol as defined in claim 1 per each part by weight of a thiobis phenol defined in claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,745,117 Dated July 10, 1973

Inventor(s) TAMOTSU FUJISAWA et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 6 - replace "Daiko" with --Daikyo-- .

Column 3, line 38 - after Example No. "12", add an asterisk.

Column 4, line 34 - in Table 2, Note 1, replace "0.05%" with --0.50%-- .

Column 4, Table 3, second column heading - after "weight", delete the comma.

Column 4, Table 3, second column, line 2 - replace "(0.25)" with --(0.5)-- .

Column 4, Table 3, second column, Example 44 - replace "(0.25)" with --(0.5)-- .

Column 4, Table 3, second column, Example 47 - replace "(0.1)" with --(0.2)-- .

Column 4, Table 3, second column, Example 51 - after "thiobis", replace "(2'6-" with --(2,6- -- .

Column 6, line 1 (Claim 3) - replace "4,4'-thiobis" with --4,4'-dithiobis-- .

Column 6, line 1 (Claim 3) - delete "butyl-".

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Column 4, Table 3, second column, Example 47 - replace "(0.1)" with --(0.2)-- .

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