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(54) **Lubricating oil composition containing sediment-reducing additive.**

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Lubricating Oil Composition Containing Sediment-Reducing Additive

This invention relates to storage-stable lubricating oil compositions containing an additive package which provides both dispersant and friction modification properties. More particularly, this invention relates to a formulated lubricating oil composition containing a polycarboxylic acid-glycol ester friction modifier and an alkenyl succinimide dispersant having a reduced tendency to form sediment upon starage.

Lubricating oil compositions which contain ashless dispersants and polycarboxylic acid-glycol esters as friction-reducing components and which may also contain sorbitan mono-oleate are known in the art and are disclosed, for example, in U.S, Patent N° 4105571, issued August 8, 1978 to Shaub *et al.* The oil-soluble alkenyl succinimide dispersants, particularly polyisobutenyl succinimide dispersants, are well known and are disclosed in U.S. Patent N° 3172892, issued March 9, 1965 to Le Suer *et al.*, and U.S. Patent N° 3933659, issued January 20, 1976 to Lyle *et al.*

It is known that lubricating oil compositions containing the aforesaid alkenyl succinimide dispersants and polycarboxylic acid-glycol ester friction modifiers offer a number of advantageous properties, however, a problem frequently encountered is the tendency of appreciable quantities of sediment to form upon storage of formulated compositions containing these additives and other conventionally employed additives, especially metal-containing additives. The present invention deals with this problem by providing additives found effective in stabilizing such compositions against sediment formation, the stabilizer additives being certain polyol-fatty acid esters.

Shaub *et al.* in U.S. Patent N° 4105571 disclose that incompatibility problems of zinc dihydrocarbyl dithiophosphate and glycol ester friction-reducing components can be resolved by pre-dispersing either component in an ashless dispersant prior to combining them in the lubricating oil formulation; however, Shaub *et al.* do note that formulations containing dispersants based on a reaction product of polyisobutenyl succinic anhydride and polyamine exhibited evidence of storage instability and suggested that an increased amount of dispersant may be necessary to maintain compatibility. The present invention deals with this problem by providing a stabilizer additive found effective in compatibilizing the compositions disclosed herein or enhancing the compatibility of said components.

In accordance with the present invention, there are provided storage-stable lubricating oil compositions having a reduced tendency to form sediment comprising–

(*a*) a polycarboxylic acid-glycol ester friction-reducing component, in an amount of 0.01 to 2% by weight,

(*b*) an oil-soluble alkenyl succinimide or borated alkenyl succinimide dispersant in an amount of 0.1 to 10% by weight, and

(*c*) an oil-soluble stabilizer additive which is a glycerol partial mono- or diester of oleic linoleic or palmitoleic acid or a mixture of said acids, in an amount effective to reduce the tendency of said lubricating oil formulation to form sediment.

The term lubricating oil composition as used herein is meant to refer to fully formulated compositions intended for use, for example, as crankcase motor oils which contain a number of conventionally used additives in the usual amounts, especially oxidation inhibitors, rust inhibitors, viscosity index improvers, such as olefin copolymers, pour depressants, oil-soluble detergent additives, such as the neutral and basic metal phenates, sulfurized phenates and sulphonates, such as the calcium and magnesium sulfurized phenates and sulphonates, as well as the zinc dialkyl dithiophosphates which are useful antioxydant and antiwear additives. It is believed that the metal-containing additives such as the normal and basic metal sulphonates, phenates and sulfurized phenates and metal dithiophosphates contribute to the tendency of lubricating oil compositions to form sediment when in the presence of the ester friction-reducing components and alkenyl succinimide dispersant. The metal phenates and sulphonates noted above are typically employed in amounts of from about 2 to 5% by weight and metal dithiophosphates are usually found in fully formulated lubricating oil compositions in amounts from about 1 to 3% by weight.

The friction-reducing esters are generally derived from the esterification of a polycarboxylic acid with a glycol and may be partial esters or diesters of the formulas:

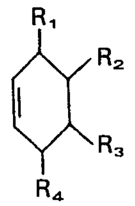
$$HO-R'-OOC-R-COOH$$
$$\text{and } HO-R'-OOC-R-COOR''-OH$$

wherein R is the hydrocarbon radical of the acid and R' and R" is either the hydrocarbon radical of an alkane diol or the oxyalkylene radical from an oxaalkane diol as defined hereinbelow. The polycarboxylic acid may be an aliphatic saturated or unsaturated acid and will generally have a total of about 24 to 90, preferably about 24 to 60 carbon atoms, and about 2 to 3, preferably about 2 carboxylic acid groups with at least about 9 carbon atoms, preferably about 12 to 42, especially 16 to 22 carbon atoms between the carboxylic acid groups. Generally about 1 to 3 mol of glycol, preferably 1 to 2 mol of glycol, are used per mole of acid to provide either a complete or partial ester.

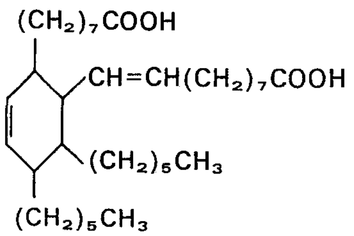
Also, esters can be obtained by esterifying a dicarboxylic acid or mixture of such acids with a diol or mixture of diols, in which case R would then be the hydrocarbon radical of the dicarboxylic acid and R' and R" would be the hydrocarbon radicals associated with the diol or diols.

The friction-reducing esters are used in amounts ranging from 0.01 to 2% by weight, more preferably 0.05 to 0.5% by weight based upon the overall weight of the lubricating oil composition, more preferably, formulations containing 0.1 to 0.3% by weight are highly effective.

Especially preferred are the dimer acid ester friction-reducing esters. The term dimer acid used herein is meant to refer to those substituted cyclohexene dicarboxylic acids formed by a Diels-Alder-type reaction which is a thermal condensation of C_{18} to C_{22} unsaturated fatty acids, such as tall oil fatty acids, which typically contain about 85 to 90% oleic or linoleic acids. Such dimer acids typically contain about 36 carbon atoms. The dimer acid structure can be generalized as follows:



with two of the R groups being carboxyl groups and two being hydrocarbon groups depending upon the condensation of the carboxylic acid has occured. The carboxyl groups can be:
$-(CH_2)_8COOH$; $-CH=CH(CH_2)_8COOH$; $(CH_2)_7COOH$; $-CH_2-CH=CH(CH_2)_7COOH$; $-CH=CH(CH_2)_7COOH$;
and the hydrocarbon terminating group can be represented by: $CH_3(CH_2)_4-$; $(CH_3)(CH_2)_5-$; $CH_3(CH_2)_7-$; $CH_3(CH_2)_4CH=CH-$; $CH_3(CH_2)_4CH=CH-CH_2-$;
and the like. The dimer of linoleic acid which is the preferred embodiment can be expressed in the following formula:



Also the term dimer acid as used herein necessarily includes products containing up to about 24% by weight trimer, but more typically about 10% by weight trimer since, as is well known in the art, the dimerization reaction provides a product containing a trimer acid having molecular weight of about three times the molecular weight to the starting fatty acid.

The polycarboxylic acids or dimer acids noted above are esterified with a glycol, the glycol being an alkane diol or oxaalkane diol represented by the formula $HO(RCHCH_2O)_xH$, wherein R is H or CH_3 and x is about 2 to 100, preferably 2 to 25 with ethylene glycol and diethylene glycol particularly preferred. A preferred embodiment is formation of the ester with about 1 to 2 mol of glycol per mole of dimer acid or polycarboxylic acid, such as the ester of diethylene glycol with dimerized linoleic acid, preferably from 0.1 to 0.3% by weight of this compound is used.

The oil-soluble alkenyl succinimide ashless dispersants are those formed by reacting a polyalkenyl succinic acid or anhydride with a polyalkyleneamine. Preferably the alkenyl group is derived from a polymer of a C_2 to C_5 monoolefin, especially a polyisobutylene where the polyisobutenyl group has a number average molecular weight of about 700 to about 5,000, more preferably about 900 to 1,500. The polyamines may be represented by the formula $NH_2(CH_2)_n-(NH(CH_2)_n)_m-NH_2$, wherein n is 2 to 3 and m is 0 to 10. Illustrative are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, which is preferred, pentaethylene hexamine and the like, as well as mixtures of such polyamines. These amines are reacted with the alkenyl succinic acid or anhydride in ratios of about 1:1 to 10:1 mol of alkenyl succinic acid or anhydride to polyamine.

The borated alkenyl succinimide dispersants are also well known in the art as disclosed in U.S. Patent N° 3254025. These borated derivatives are provided by treating the alkenyl succinimide with a boron compound selected from the class consisting of boron oxides, boron halides, boron acids and esters thereof in an amount to provide from about 0.1 atomic proportion of boron to about 10 atomic proportions of boron for each atomic proportion of nitrogen in the dispersant. The borated product will generally contain about 0.1 to 2.0, preferably 0.2 to 0.8% by weight boron based upon the total weight of the borated dispersant. The boron is considered to be present as dehydrated boric acid polymers attaching as the metaborate salt of the imide. The boration reaction is readily carried out by adding from about 1 to 3% by weight, based on the weight of dispersant, of said boron compound, preferably boric acid, to the dispersant as a slurry in mineral oil and heating with stirring as from about 135 to 165°C for from 1 to 5 h followed by nitrogen stripping and filtration of the product.

These alkenyl succinimide ashless dispersants and borated derivatives thereof are used in lubricating oil compositions in amounts ranging from 0.1 to 10% by weight, preferably 0.5 to 5%, based upon the total weight of the finished composition.

In the stabilizer additives used in the present invention, partial ester means that at least one hydroxy group remains unreacted. Preferably 1 to 3 free OH groups are present such as an average of 1.5 to 2.5 free hydroxy groups. Such compounds are, *per se*, known in the art and it is only their use as a stabilizing agent in a formulated composition containing both the ester friction modifier and alkenyl succinimide dispersant or borated dispersant derivative thereof which is the basis of the present invention. Preferred additives are the mixtures of glycerol mono- and diesters of oleic acid.

The quantity of sediment-reducing amount of additive stabilizer of the present invention which is used in a lubrification oil formulation is best expressed relative to the amount of the ester friction-reducing additive which is present. The broad ratio is 2 to 20 parts by weight of additive stabilizer per part by weight of ester friction-reducing additive with the preferred ratio being about 2 to 12 parts by weight of stabilizer additive per part by weight of friction-reducing ester.

While the method of addition of the stabilizer additive is largely a function of the exact composition of the total finished formulation, it is generally preferable to provide a blend of stabilizer additive, friction-reducing ester and dispersant by admixing same at moderately elevated temperatures, not greater than 150°F (66°C) and incorporating this blend into the lubricating oil formulation either prior to or subsequent to the addition of other additives in accordance with blending techniques known in the art.

The lubricating oil base stock employed herein are those customarily used: The term lubricating oil includes not only the petroleum hydrocarbon paraffinic, naphthenic, and aromatic oils of lubricating viscosity, but also synthetic oils, such as polyethylene oils, esters of dicarboxylic acids, complex ester oils, polyglycol, and alcohol alkyl esters of carbonic or phosphoric acids, polysilicones, fluorohydrocarbon oils, and the like. Preferred base stocks are mineral hydrocarbon oils of a paraffinic nature, especially those having a viscosity of about 20 to 100 cPo (0.2 to 1 × 10^{-4} m^2s^{-1})/min (100°F [38°C]), and blends of such mineral paraffinic oils.

The additives of the present invention are generally effective in substantially eliminating all but traces of sediment when the lubricating oil formulation contains the usually preferred amounts of friction-reducing ester component, that is, about 0.05 to 0.3% by weight and therefore, formulations prepared in accordance with the present invention which contain these amounts of friction-reducing ester component are particularly preferred. For formulations containing more than about 0.3% by weight of ester component, there will be in most cases a substantial reduction in the amount of sediment observed after centrifuging as opposed to a complete elimination to trace levels.

Example:

Lubricating oil formulations were prepared containing the dimer acid ester friction modifier and the alkenyl succinimide dispersant to which were added the sediment-reducing additives of the present invention. The formulation was a standard 10 W-SAE quality automotive lubricating oil composition containing a zinc dialkyl dithiophosphate, overbased metal sulphonate, rust inhibitor, and viscosity index improver in typical proportions. At this point the formulation was storage-stable with no evidence of sediment formulation. To this was added 0.1% by weight of a friction modifier being the ester of a dimerized linoleic acid and diethylene glycol and 5% by weight of the action product of 2.1 mol polyisobutenyl ($\overline{M}n$=1300) succinic anhydride (Sample N° 103) and 1 mol of alkylene polyamine to provide the Base Formulation. The polyamine had a composition approximating tetraethylene pentamine and is available under the trade name DOW E-100 from Dow Chemical Company, Midland, Michigan. Samples (100 ml, calibrated test tube) of this Base Formulation were centrifuged for 8, 16, and 24 h at 1,900 tr/min at room temperature and thereafter, samples containing the sediment-reducing additives of this invention were also tested for compatibility by centrifuging under the same conditions. The volume percent sediment was measured on the basis of the sediment observed in a calibrated test tube which contained the 100-ml samples and the result are set forth in the following Table 1.

Table 1
After Centrifuging (Vol. %)

	8 h	16 h	24 h
Base	.20	.50	3.00
Base + Glyceride (Examples 1 and 1A)	Trace	Trace	Trace

Example 1:

0.26% by weight liquid mixture of mono- and diglyceride of oleic acid, 55% by weight monoester, 130 cPo (1.3 × 10^{-1} Pa·s) viscosity at 25°C, sold as ATMOS®300 by ICI America, Inc.

Example 1A:

Example 1 was repeated using 0.56% by weight of the same glyceride with the same results after centrifuging.

Example 2:

A formulation was prepared similar to the Base Formulation of Example 1 except that 0.3% by weight of the dimer acid ester friction-reducing component was used. The Base Formulation showed about a 3.0 vol. % sediment formation after 24 h centrifuging. After addition of 1.25% by weight of the same glyceride of Example 1, the formation was stable after 24 h centrifuging.

Example 3:

Example 2 was repeated with the same results using the same stabilizer additive in the same amount except that the Base Formulation contained a borated alkenyl succinimide dispersant prepared by reacting the dispersant of the Base Formulation with a slurry of 1.4 mol of boric acid in mineral oil over a 3-h period at 135 to 165°C followed by 4 h of nitrogen stripping. The final product contained 1.5% by weight nitrogen and 0.3% by weight boron and had a $\overline{M}n$ of about 3,000.

Claims

1. A storage-stable lubricating oil composition having a reduced tendency to form sediment comprising a lubricating oil containing—

(*a*) 0.01 to 2% by weight, based on the total weight of the finished composition, of a polycarboxylic acid-glycol ester friction-reducing component;

(*b*) 0.1 to 10% by weight, based on the total weight of the finished composition, of an oil-soluble alkenyl succinimide or borated alkenyl succinimide dispersant; and

(*c*) an oil-soluble stabilizer additive which is a glycerol partial mono- or diester of oleic, linoleic or palmitoleic acid or a mixture of said acids.

2. The composition of Claim 1, wherein there is present 0.05 to 0.5% by weight of said (*a*) component based on the total weight of the lubricating oil composition.

3. The composition of Claim 1 or 2, wherein said (*c*) component is a mixture of glycerol mono- and diesters of oleic acid.

4. The composition of Claims 1 to 3, therein the weight ratio in parts by weight of said (*c*) component to said (*a*) component is from 2 to 20 parts by weight of said (*c*) component per part by weight of said (*a*) component.

5. The composition of Claims 1 to 4, wherein said (*a*) component is diethylene glycol ester of dimerized linoleic acid present in an amount from 0.1 to 0.3% by weight, based on the total weight of the composition.

6. The composition of Claims 1 to 5, wherein said (*b*) dispersant component is a polyisobutenyl succinic anhydride-polyalkyleneamine reaction product or borated polyisobutenyl succinimide.

Revendications

1. Composition d'huile lubrifiante stable à l'entreposage, ayant une tendance réduite à la formation de sédiment, comprenant une huile lubrifiante renfermant:

a) 0,01 à 2% en poids, sur la base du poids total de la composition finie, d'un ester d'acide polycarboxylique et de glycol comme agent réducteur de friction;

b) 0,1 à 10% en poids, sur la base du poids total de la composition finie, d'un alcénylsuccinimide ou d'un alcénylsuccinimide boraté soluble dans l'huile comme agent dispersant, et

c) un additif stabilisant soluble dans l'huile qui est un monoester ou un diester partiel de glycérol d'acide oléique, d'acide linoléique ou d'acide palmitoléique ou d'un mélange desdits acides.

2. Composition suivant la revendication 1, qui contient 0,05 à 0,5% en poids dudit composant (a) sur la base du poids total de la composition d'huile lubrifiante.

3. Composition suivant l'une des revendications 1 ou 2, dans laquelle le composant (c) est un mélange de monoesters et de diesters de glycérol de l'acide oléique.

4. Composition suivant l'une des revendications 1 à 3, dans laquelle le rapport en poids, en parties en poids, dudit composant (c) audit composant (a) est de 2 à 20 parties en poids du composant (c) par partie en poids du composant (a).

5. Composition suivant l'une des revendications 1 à 4, dans laquelle le composant (a) est l'ester de diéthylèneglycol de l'acide linoléique dimérisé présent en une quantité de 0,1 à 0,3% en poids sur la base du poids total de la composition.

6. Composition suivant l'une des revendications 1 à 5, dans laquelle le dispersant (b) est un produit de réaction d'anhydride polyisobutényl-succinique et de polyalkylèneamine ou un polyisobuténylsuccinimide boraté.

Patentansprüche

1. Lagerstabile Schmierölzusammensetzung mit verringerter Neigung zur Sedimentbildung, enthaltend ein Schmieröl, welches:

a) 0,01 bis 2 Gew.-%, basierend auf dem Gesamtgewicht der Endzusammensetzung, einer Polycarbonsäure/Glykolester-Reibungsverminderungskomponente,

b) 0,1 bis 10 Gew.-%, basierend auf dem Gesamtgewicht der Endzusammensetzung, eines öllöslichen Alkenylsuccinimid- oder borierten Alkenylsuccinimiddispersionsmittels, und

c) einen öllöslichen Stabilisatorzusatz, der ein Glycerinpartialmono- oder -diester von Ölsäure, Linolsäure oder Palmitoleinsäure oder einem Gemisch dieser Säuren ist,

enthält.

2. Zusammensetzung nach Anspruch 1, worin 0,05 bis 0,5 Gew.-% der Komponente (a), basierend auf dem Gesamtgewicht der Schmierölzusammensetzung, vorhanden sind.

3. Zusammensetzung nach einem der Ansprüche 1 oder 2, worin die Komponente (c) ein Gemisch von Glycerinmono- und -diestern von Ölsäure ist.

4. Zusammensetzung nach den Ansprüchen 1 bis 3, worin das Gewichtsverhältnis in Gewichtsteilen der Komponente (c) zu der Komponente (a) von 2 bis 20 Gewichtsteilen der Komponente (c) pro Gewichtsteil der Komponente (a) beträgt.

5. Zusammensetzung nach den Ansprüchen 1 bis 4, worin die Komponente (a) Diethylenglykolester von dimerisierter Linolsäure ist und in einer Menge von 0,1 bis 0,3 Gew.-%, basierend auf dem Gesamtgewicht der Zusammensetzung, vorhanden ist.

6. Zusammensetzung nach den Ansprüchen 1 bis 5, worin die Dispersionsmittelkomponente (b) ein Polyisobutenylsuccinsäureanhydridpolyalkylenaminreaktionsprodukt oder boriertes Polyisobutenylsuccinimid ist.