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(54) Lubricant composition with stabilized metal detergent additive and friction reducing ester component.

(57) Oils with metal sulfonate or sulfurized phenate detergents and friction reducing dicarboxylic esters are stabilized against haze or sediment formation by treatment of this oil solution of metal additive, prior to ester incorporation, with a phosphosulfurized polyisobutylene or a polyisobutenyl succinic anhydride at 55° to 225°C for 2-30 hours.

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This invention relates to oil compositions which contain both an overbased metal detergent additive and a glycol ester friction modifier. More particularly, this invention relates to a method for formulating such compositions wherein the formation of haze and sediment due to the imcompatibility of these additives is overcome.

Lubricating oil compositions containing metal detergent additives being either the normal or basic (overbased) magnesium or calcium sulfurized phenates or sulfonates are well known in the art and are employed in various motor oil formulations. Formulating these metal detergent additives with other ingredients in a finished lubricating oil blend has been known to create compatibility problems, specifically the formation of sediment, separation of phases, visible precipitation or haze and similar problems which are evidence of incompatibility or unwanted interaction of components.

Resolution of this problem through techniques known in the art is represented by U.S. Patent 3,714,042, issued January 30, 1973 to Greenough, which discloses the treatment of overbased complexes with a high molecular weight aliphatic carboxylic acid or anhydride at elevated temperatures. U.S. Patent 3,965,017, issued to Burnop et al discloses stabilization through addition of small proportions of a monocarboxylic acid, anhydride or salt or the reaction product of a hydrocarbon with P_2S_5 and a glycol or ether alcohol.

Lubricant compositions containing the polycarboxylic acid-glycol ester friction modifier additive used in the compositions of the present invention are disclosed in U.S. Patent 4,105,571 issued to Shaub et al.

The present invention is concerned with resolution of the specific problem of incompatibility encountered when lubricating oil formulations are prepared which contain both a metal or overbased metal sulfonate or a sulfurized phenate detergent additive, particularly where the metal is calcium or magnesium, and small proportions of a glycol-polycarboxylic acid ester friction reducing additive.

In accordance with the present invention, there is provided a lubricating oil composition having a reduced tendency toward sediment formation, which comprises a glycol-polycarboxylic acid ester friction reducing additive and a metal detergent additive being a metal or overbased metal sulfonate or sulfurized phenate, which composition is prepared by a process comprising the steps of:

(a) providing a lubricating oil mixture containing a lubricating oil base stock containing about 0.1 to 10 percent by weight of a metal or overbased metal sulfonate or sulfurized phenate detergent additive;

(b) treating said mixture by reacting said metal detergent additive with from about 50 to 100 percent by weight, based upon the weight of the metal detergent additive, with either (i) a phosphosulfurized polyisobutylene or (ii) a polyisobutenyl succinic anhydride at temperatures of from about 55°C to about 225°C for a period of from about 2 to 30 hours; and

(c) thereafter, adding to said treated mixture about 0.01 to about 2.0 percent by weight, based on the total weight of the composition, of said glycol ester friction modifier additive, whereby said composition exhibits a reduced tendency toward phase separation or sediment or haze formation.

The metal detergent additives used in the present invention are those metal or overbased metal sulfonate or sulfurized phenate oil-soluble additives which are well known in the art. The metal sulfonates are obtained from sulfonic acids derived from sulfonating natural or synthetic hydrocarbons, such as by treating oil base stocks with concentrated or fuming sulfuric acid or by sulfonating alkylated aromatic hydrocarbons. The hydrocarbyl sulfonate of these metal detergent additives is derived from petroleum sulfonates and includes alkyl, alkylaryl and aryl sulfonates and mixtures thereof having a molecular weight of from about 300 to 1,000, such as barium nonylbenzene sulfonate, magnesium dodecylbenzene sulfonate and the like. The sulfonates are usually the alkaline earth metal sulfonates, usually calcium, barium, or magnesium, but can also be alkali metal sulfonates, such as sodium sulfonates. Overbased sulfonates are those which contain metal base in excess that is required for simple neutralization. In preparing such overbased materials, the sulfonic acid is typically reacted with an excess of metal base and the excess base is usually neutralized with an acidic gas, such as carbon dioxide. Such overbased sulfonates have a total base number (ASTM-D-664) of about 50 to 500.

The sulfurized phenates are the metal salts of sulfurized alkyl phenols, which contain about 2 to 14 percent by weight sulfur based on the weight of the sulfurized alkyl phenols. Such materials are well known in the art and are derived from alkylated phenols, wherein the alkyl is C_5-C_{40}, such as t-amyl phenol, t-octyl phenol, nonylphenol, di-t-octyl phenol and phenols alkylated with suitable polymers of up to 40 carbon atoms obtained from propylene, butylene, amylenes or mixtures thereof. The sulfurized phenols are prepared by well-known methods, for example, by reacting the alkylated phenol with sulfur monochloride, sulfur dichloride or elemental sulfur.

The metals employed for providing the phenate salts are typically alkali metal, alkaline earth metal or magnesium, principally calcium or magnesium. Overbased phenates are prepared by the process comprising reacting the phenol with excess base and the excess is neutralized with carbon dioxide. Typical overbased metal sulfurized phenates will have a total base number (ASTM-D-664) of about 50 to 100.

The treatment step of the present invention generally comprises incorporating the metal detergent additive into a lubricating oil and conducting a reaction for about 2 to 30 hours at temperatures of from about 55°C to 225°C with either a phosphosulfurized polyisobutylene or with a polyisobutenyl succinic anhydride, and 25-100 percent, preferably 50-100, percent by weight of these materials are used based upon the weight of the metal detergent additive present.

When employing a phosphosulfurized polyisobutylene, it is preferable in most cases to conduct the treatment step of the present invention at relatively higher temperatures and longer periods of time. Thus, the preferred treatment conditions for P_2S_5-polyisobutylene treatment are temperatures of about 100°C to 200°C and a treatment period of about 10 to 25 hours, particularly when the metal additive is an overbased calcium or magnesium sulfurized phenate.

When the polyisobutenyl succinic anhydride is employed, preferred conditions of treatment in accordance with this invention are temperatures of about 60°C to 85°C for about 2 to 7 hours.

Phosphosulfurized polyisobutylenes useful in the present invention are prepared by methods well known in the art comprising the reaction of sulfides of phosphorous with polyisobutylene at elevated temperatures. While P_2S_5 is preferred, P_2S_3, P_4S_3 and P_4S_5 are also useful as well as mixtures thereof, as well as mixtures of elemental phosphorous and sulfur. The reaction is carred out at about 90°C to 315°C, preferably 150°C, to 290°C, using about 1 to 5 molar proportions of polyisobutylene to 1 molar proportion of phosphorous sulfide. The reaction is usually continued until the maximum amount of sulfur or phosphorous sulfide has been added but this is not essential to provide a useful product. Typical reaction times are about 2 to 10 hours. Generally, the polyisobutylenes have a molecular weight of about 500 to 25,000, preferably 800 to 2,000. Particularly useful are polyisobutylenes of 700 to 1500 molecular weight reacted with about 10 to 15 percent by weight of P_2S_5.

The polyisobutenyl succinic anhydrides useful herein for treating the metal detergent additives are also known and are disclosed in the number of references, such as U.S. Patent 3,288,714, issued to Osuch. These are oil-soluble materials, which have desirable additive properties themselves, principally as dispersants, prepared by reacting maleic anhydride with a polyisobutylene polymer having a molecular weight of about 500 to 2,000. Particularly preferred for use as treating agents in the present invention are those polyisobutenyl succinic anhydrides wherein the polyisobutenyl group has a number average molecular weight of about 700 to 1,500.

The lubricating oil base stock employed herein generally comprises a hydrocarbon mineral oil of lubricating viscosity including paraffinic, naphthenic and aromatic oils preferably a mineral paraffinic oil having a viscosity of about 20 to 100 cs. min. (100°F) and blends of such mineral paraffinic oils. Synthetic oils may be used provided the conditions of treatment do not adversely affect such synthetic oils by causing an unwanted side reaction.

The finished formulation then may be prepared by incorporating into the treated composition the friction reducing polycarboxylic acid glycol ester which is employed in amounts of about 0.01 to 2.0 percent preferably 0.05 to 0.3 percent by weight, typically, 0.1 to 0.3 percent by weight based upon the total weight of the composition being used. These friction reducing esters are described in more detail hereinbelow.

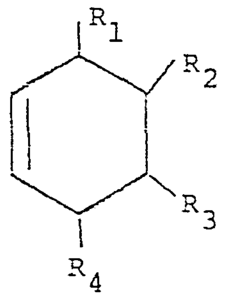
The friction reducing esters are generally derived from the esterification of a polycarboxylic acid with a glycol and may be partial esters or diesters of the formulas:

HO-R'-OOC-R-COOH and HO-R'-OOC-R-COOR"-OH

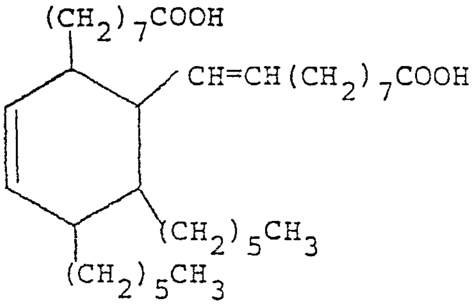
wherein R is the hydrocarbon radical of the acid and R' and R" is either the hydrocarbon radical of an alkane diol or the oxyalkylene radical from an oxa-alkane diol as defined hereinbelow. The polycarboxylic acid may be an aliphatic saturated or unsaturated acid and will generally have a total of about 24 to 90, preferably about 24 to 60, carbon atoms and about 2 to 3, preferably about 2, carboxylic acid groups with a least about 9 carbon atoms, preferably about 12 to 42, especially 16 to 22 carbon atoms between the carboxylic acid groups. Generally about 1-3 moles of glycol, preferably 1-2 moles of glycol, is used per mole of acid to provide either a complete or partial ester. Esters within the foregoing formula can also be prepared by reaction of the acid with 1 mole or more of ethylene oxide.

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

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}-C_{22} unsaturated fatty acids, such as tall oil fatty acids which typically contain about 85 to 90 percent 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 how the condensation of the carboxylic acid has occurred. The carboxyl groups can be $-(CH_2)_8COOH$;$-CH=CH(CH_2)_7COOH$;$-(CH_2)_7COOH$; $-CH_2CH=CH(CH_2)_7COOH$;$-CH=CH(CH_2)_7COOH$ and the hydrocarbon terminating group can be represented by: $CH_3(CH_2)_4-$; $CH_3(CH_2)_5-$;$CH_3(CH_2)_7$;$-CH_3(CH_2)_4CH=CH-$;$CH_3(CH_2)_4CH=CH\ CH_2-$; $CH_3(CH_2)_4CH=CH\ CH_2-$; 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 percent by weight trimer, but more typically about 10 percent 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 of the starting fatty acid.

The polycarboxylic acids or dimer acids noted above are esterified with a glycol, the glycol being an alkane diol or oxa-alkane 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 moles of glycol per mole of dimer acid or polycarboxylic acid, such as the ester of diethylene glycol with dimerized linoleic acid.

Numerous other additives will of course normally be included in a finished lubricating oil composition such as detergents and dispersants, oxidation and rust inhibitors, viscosity index improvers, pour depressants, anti-wear agents and the like and these may be added prior to or subsequent to the addition of the friction reducing ester component.

EXAMPLES

Formulations were prepared which demonstrated the incompatibility of the metal detergent additive with a dimer acid ester friction modifier which in each formulation was diethylene glycol ester of dimerized linoleic acid. In each formulation set forth in Table I, the composition was cloudy with visible separation of phases after standing for several days both at room temperature and at 65°C. The base oil in each case was Solvent 150 Neutral oil, a mineral paraffinic oil having a viscosity of 31 cS. min. at 37.8°C.

TABLE I

Component	Formulation - Weight Percent				
	A	B	C	D	E
Overbased Ca Sulfurized Phenate (1)	1.0	-	-	-	-
Overbased Mg Sulfurized Phenate (2)	-	0.8	-	-	-
Overbased Mg Sulfonate (3)	-	-	1.04	-	-
Overbased Ca Sulfonate (4)	-	-	-	-	1.5
Ca Sulfurized Phenate (5)	-	-	-	1.5	-
Base Oil	98.9	99.1	98.86	98.4	98.4
Friction Modifier	0.1	0.1	0.1	0.1	0.1

In each formulation of Table I, in the absence of the friction modifier additive the formulations were clear with no evidence of instability after storage for equivalent periods of time under the same conditions. Total base numbers reported are according to ASTM-D-664.

(1) Overbased calcium sulfurized dodecyl phenate sulfide having a total base number of 250.

(2) Overbased magnesium sulfurized nonylphenate, nonylphenol sulfide having a total base number of 250.

(3) Overbased magnesium alkyl sulfonate having a total base number of 395.

(4) Overbased calcium alkyl sulfonate having a total base number of 300.

(5) Calcium sulfurized dodecyl phenate having a total base number of 135.

A number of stabilized formulations were prepared by first treating an oil concentrate containing 20-30 wt. percent of the metal detergent additive with a P_2S_5-polyisobutylene (mol. wt. 780) and then blending with the base oil and friction modifier to provide the finished formulation. These are set forth in Table II which includes the various treatment times and temperatures used; all formulations were clear with no evidence of instability upon standing for 1 month at room temperature and 1 month at 65°C. The metal additives and friction modifier are the same as those reported in Table I.

Similarly, metal detergent additives were treated with two types of polyisobutenyl succinic anhydrides; formulations A & B used $\bar{M}n$=1,000 and Sap No. 112 and formulations C & D used $\bar{M}n$=1,300 and Sap. No. 103 under varying conditions of time and temperature and, thereafter, the treated materials were blended into the formulations reported in Table III each of which remained clear upon storage for 1 month at room temperature and 1 month at 65°C with no instability apparent. Again, the base oil, additives and friction modifiers are those identified in the prior examples.

TABLE II

Component	A	B	C	D	E
	Formulation - Weight Percent				
Overbased Ca Sulfurized Phenate	1.0	-	-	-	-
Overbased Mg Sulfurized Phenate	1	10	-	-	-
Overbased Mg Sulfonate	-	-	1.0	-	-
Ca Sulfurized Phenate	-	-	-	1.0	-
Overbased Ca Sulfonate	-	-	-	-	1.0
P_2S_5 - Polyisobutylene	0.5	10	0.1	0.5	0.5
Base Oil	98.5	79.8	98.8	98.4	98.4
Friction Modifier	0.1	0.2	0.1	0.1	0.1
	Treatment Conditions				
Hours	20	24	7	14	17
Temperature °C	152°	200°	59°	68°	64°

TABLE III

Component	A	B	C	D
	Formulation - Weight Percent			
Overbased Mg Sulfurized Phenate	1.0	-	1.0	-
Overbased Ca Sulfurized Phenate	-	1.0	-	1.0
Polyisobutenyl Succinic Anhydride	0.5	0.2	0.5	0.5
Base Oil	98.4	98.7	98.4	98.4
Friction Modifier	0.1	0.1	0.1	0.1
	Treatment Conditions			
Hours	4	5	24	24
Temperature °C	64°	70°	82°	82°

Instead of carrying out the treatment of the detergent additive in a lubricating oil, the same results are obtained by carrying out the treatment in a lubricating oil concentrate wherein said detergent additive is present in amounts of 20 to 50 wt. percent, based on the total oil composition, the base oil comprising 50 to 80 percent of the composition, or a portion of the oil may be replaced by other additives, such as viscosity index improver, pour depressants, dispersants, etc. Thus, 0.1 to 50 wt. percent of the detergent additive admixed with the oil can be used in the reaction with said phosphosulfurized polyisobutylene or anhydride reactants.

WHAT WE CLAIM IS:

1. An oil composition comprising a lubricating oil base stock, a polycarboxylic acid glycol ester friction modifier additive and a metal or overbased metal sulfonate or sulfurized phenate detergent additive which composition is prepared by a process comprising the steps of: (a) providing a mixture containing a lubricating oil base stock and about 0.1 to 50 percent by weight of the metal detergent additive; (b) treating said mixture by reacting it with 25 to 100 percent by weight, based on the weight of the metal detergent additive, with either a phosphosulfurized polyisobutylene or a polyisobutenyl succinic anhydride at temperatures of from about 55° to about 225°C for about 2 to 30 hours, and (c) thereafter adding to said treated mixture about 0.01 to about 2.0 percent by weight, based on the total weight of the composition, of the glycol ester friction modifier additive, whereby said composition exhibits a reduced tendency toward sediment formation or phase separation.

2. The composition of claim 1 wherein the metal detergent additive is an overbased calcium or magnesium sulfonate.

3. A composition of claim 1 wherein the metal detergent additive is an overbased calcium or magnesium sulfurized phenate.

4. The composition of claims 1 or 2 wherein said treatment step is conducted with a polyisobutenyl succinic anhydride wherein the polyisobutenyl group has a molecular weight of from about 700 to 1,500.

5. The composition of claims 1-4 wherein the friction modifier is the diethylene glycol ester of the dimer acid of linoleic acid.

6. The composition of claim 5 wherein the concentration of said glycol ester is from about 0.05 to about 0.3 weight percent.

7. The composition of claims 1-3 wherein said treatment step is conducted with a polyisobutylene of 700 to 1500 molecular weight phosphosulfurized with P_2S_5.

8. The composition of claim 7 wherein said treatment step is conducted at a temperature of from about 100°C to 200°C for a period of about 10 hours to 25 hours.

9. The composition of claim 4 wherein the treatment is conducted at a temperature of from about 60° to 85°C for about 2 to 7 hours.

10. The composition of claims 1-9 wherein said treatment is carried out on a mixture containing said lubricating oil base stock and about 0.1 to 10 percent by weight of said metal detergent additive, using 50 to 100 percent by weight, based on the weight of said metal detergent additive, of said phosphosulfurized polyisobutylene or of said anhydride.