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3,368,971

## LUBRICATING OIL COMPOSITIONS

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## ABSTRACT OF THE DISCLOSURE

Increased corrosion resistance is imparted to lubricating oils by the addition of a mixture of (1) the reaction product of an alkenyl succinic anhydride with diethanolamine, and (2) an oil-soluble calcium compound such as calcium phenates or calcium sulfonates.

This invention relates to lubricants having improved antirust properties. In particular, this invention relates to lubricants containing an ashless dispersant and an oil soluble calcium compound.

Engine parts will rust if they are not adequately protected from the corrosive effects of water and acids. Such rust is especially critical in close tolerance operating parts such as hydraulic valve lifters. The rust problem is particularly troublesome during storage or operation at low temperatures.

Although petroleum oils do offer some protection against rust, they do not have sufficient antirust properties. Therefore, oil additives are frequently used to supply the required rust protection.

Low temperature engine service also leads to sludge formation in the engine. This results from partially oxidized combustion products being carried into the lubricating oil with the "blowby gases" leaking past the piston rings in the engine cylinders. These partial oxidation products are believed to lead to engine sludge or deposits through a polymerization process. Some of the deposits appear in the engine as varnish, while others drop out of solution as sludge. This sludge and varnish problem has resulted in the inclusion of dispersants in lubricating oils.

Of recent years, a trend towards ashless or non-metallic dispersants has evolved. Some of these are reaction products of alkenyl succinic anhydride or acids with various amines forming alkenyl succinimides, and will be referred to as "amide type" dispersants. When these amide type dispersants are used in lubricating oils they are frequently used in conjunction with an antirust agent. These antirust agents are usually calcium, barium or other metal phenates or sulfonates. It has now been discovered that when a particular class of dispersant is employed in combination with a soluble calcium compound, not only are excellent dispersant properties obtained, but a significant increase in rust protection is obtained than would be obtained from the same amount of calcium compound used in combination with a conventional amide type dispersant.

An object of this invention is to provide improved lubricating oils. A further object is to provide lubricating oils having excellent dispersant and antirust properties. A still further object is to provide a combination of dispersant and oil soluble calcium compound having enhanced rust inhibiting properties.

These and other objects are accomplished by providing a lubricating oil containing a dispersing quantity of an ashless dispersant formed as the reaction product of either an alkenyl succinic anhydride or an alkenyl succinic acid with diethanol amine, and also containing from about 0.01 to 1.0 weight percent calcium as an oil soluble calcium compound.

In a preferred embodiment of this invention, the

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alkenyl group of the alkenyl succinic anhydride or acid is derived from a polybutene having a molecular weight of from about 700 to 1600.

In a more preferred embodiment, the alkenyl group is derived from a polybutene having a molecular weight of from about 900 to 1100.

In another preferred embodiment, the oil soluble calcium compound is an overbased calcium sulfonate.

The ashless dispersant used in the present compositions is derived from the reaction of an alkenyl succinic anhydride or acid with diethanol amine. These dispersants will be referred to as "DEA type dispersants." The reaction and the products formed are described in copending application Ser. No. 387,216, filed Aug. 3, 1964, now abandoned. In essence, the process consists of reacting an olefin, preferably derived from the polymerization of a low molecular weight olefin monomer, with maleic anhydride. In a preferred embodiment, the olefin is a polybutene having a molecular weight of from about 700 to 1600. About equal molar amounts of the polybutene and maleic anhydride are employed and the reaction is usually carried out in the presence of a solvent, e.g., xylene. The reactants are heated to about 200° C. in a pressure vessel and kept at this temperature for about 6 hours. They are then cooled and the solvent together with any unreacted maleic anhydride or polybutene is distilled. The resulting alkenyl succinic anhydride is then reacted with about an equal mole quantity for example, from 0.75 to 1.2 moles, of diethanol amine, employing sufficient solvent so that the reflux temperature of the reaction mass is about 180° C. As the diethanol amine reacts with the alkenyl succinic anhydride, water forms, which is distilled off together with the solvent employed. When most of the water has been removed, the remaining solvent is distilled out at reduced pressure (approximately 20 mm.), leaving the DEA type dispersant. Further details of the preparation can be obtained from application Ser. No. 387,216, which is incorporated herein by reference as if fully set forth. The following example will serve to illustrate a typical synthesis. All parts are parts by weight unless otherwise indicated.

## Example 1

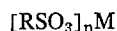
To a reaction vessel equipped with stirrer, temperature measuring means, heating means and reactant addition means is charged 876 parts of xylene, 4230 parts of polybutene and 450 parts of maleic anhydride. The vapor space above the reactants is displaced with a nitrogen atmosphere and, while stirring, the reactants are heated to a temperature of about 225° C. Pressure within the vessel is limited to 60 p.s.i.g. by periodically venting excess pressure. The reaction is maintained at this temperature for about 6 hours, following which it is cooled to about 180° C. and vented to atmospheric pressure. The xylene solvent and unreacted maleic anhydride and polybutene are then distilled out until the reactant temperature is about 250° C. The last portion of the solvent and unreacted reactants are removed by gradually reducing the pressure within the reaction vessel to about 40 mm. Following this, the alkenyl succinic anhydride formed is cooled to about 70° C., and 680 parts of xylene are added. The vessel contents are then heated to about 140° C., and 346 parts of molten diethanol amine are added over a 30 minute period. This reaction is exothermic and the temperature will rise to about 160° C. After the diethanol amine addition is complete, the vessel contents are heated to 180° C., at which point xylene together with the water formed by the reaction of the diethanol amine and alkenyl succinic anhydride will distill. The water is drained from the distillate and the xylene is allowed to return to the reaction vessel. After about 48 parts of water are re-

moved, the pressure within the reaction vessel is gradually reduced to 48 mm. Hg while maintaining the temperature at about 180° C., during which period substantially all water and xylene is removed. The resulting product is a typical DEA type dispersant.

Oil soluble calcium compounds suitable for use in the present compositions are commercially available. For example, they can be obtained from Bryton Chemical Company, New York, N.Y. Other oil soluble calcium compounds are described in U.S. Patents 2,616,904, 2,616,905, 2,616,906, 2,616,911, 2,616,924, 2,616,925, 2,695,910, 2,915,517, 3,001,981, 3,027,325, 3,146,201, and 2,835,688.

The preferred oil soluble calcium compounds are the calcium phenates or calcium sulfonates. Of these the sulfonates are more preferred. Calcium sulfonates are calcium salts of either petroleum sulfonates or synthetic sulfonates. The petroleum sulfonates are derived from the fuming sulfuric acid treatment of lubricating oils in the manufacture of medicinal or technical white oils. Chemically the natural sulfonates are mixtures of alkyl-aryl molecular structures of varying molecular weights. For the most part, they are prepared commercially in mineral oil dilutions and have an average molecular weight of from about 430 to 500.

Synthetic sulfonates are derived from the sulfonation of alkylated aromatic hydrocarbons. They differ from natural sulfonates in the numbers and type of aromatic ring structure as well as in the length and numbers of side chains attached to the aromatic ring. They may be represented by the general formula:



wherein R represents the alkaryl portion of the molecule and  $n$  is the valence of the metal M.

Calcium sulfonates are made by reacting calcium oxide, hydroxide or carbonate with a high molecular weight sulfonic acid. A preferred calcium sulfonate is one prepared in such a manner that the product is basic; that is, more equivalents of calcium are employed than there are acid equivalents in the sulfonic acid. These are called overbased calcium sulfonates. Preferred overbased calcium sulfonates have a base number of from about 25 to about 500. The more preferred calcium sulfonates have a base number of from about 100 to 400, and the most preferred have a base number of about 300. Base number is determined by ASTM Method D-974.

The DEA type dispersant should be present in the lubricating oil in a dispersing quantity. In most cases, a concentration of from 0.1 to 10 weight percent is satisfactory. A more preferred concentration range is from 0.2 to 7 weight percent, and a most preferred range is from about 1 to 4 weight percent.

The oil soluble calcium compound should be present in the lubricating oil in a rust inhibiting quantity. In general, a concentration of from 0.01 to 1.0 weight percent calcium as the oil soluble compound is satisfactory. A more preferred range is from 0.02 to 0.4 weight percent, and a most preferred range is from 0.05 to 0.3 weight percent calcium as the oil soluble calcium compound. The desired amount of DEA type dispersant, an oil-soluble calcium compound, is readily added to the lubricating oil in the form of a concentrate consisting essentially of from about 10-99 weight percent of the DEA type dispersant and from about 1-50 weight percent of calcium as an oil-soluble calcium compound.

The improved antirust-dispersant combinations of this invention are useful in a variety of oils including natural and synthetic oils. Some examples of synthetic oils are the esters of organic acids such as sebacic or phthalic acid. Specific examples of these are dioctyl sebacic, dinonyl sebacic, dieicosyl sebacic, dioctyl phthalic, didecyl phthalic or dilauryl phthalic. Other synthetic oils are the esters of phosphoric acids such as tricetyl phosphate, and the like. Further examples of synthetic oils are the poly-

ether synthetic oils such as the diphenyl ether of polyethylene glycol having a molecular weight of from about 500 to 1000. Another is the diethyl ether of a polypropylene glycol having a molecular weight of from about 1000 to 1500.

The antirust-dispersant combinations of this invention find their greatest use in hydrocarbon derived oils including hydraulic oils, functional fluids such as automatic transmission fluid, and lubricating oils for turbines, diesel engines and spark ignited engines, both two and four cycle. The additive compositions are especially useful in automotive type lubricating oils. Such oils may contain other additives such as polymethacrylate VI improvers, cloud and pour-point depressants, antioxidants such as zinc dithiophosphate, 2,6-di-tert-butylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,6-di-tert-butyl-4-methylphenol, N,N-dimethyl(3,5-di-tert-butyl-4-hydroxybenzyl)amine, and the like. Some examples of these oil compositions are as follows. All parts are parts by weight unless otherwise indicated.

#### Example 2

To 1000 parts of a solvent refined Mid-Continent lubricating oil containing 0.08 part zinc as zinc dithiophosphate is added about 50 parts of a polymethacrylate VI improver and 0.7 part of calcium as a calcium sulfonate having a molecular weight of 940 and 50 parts of a DEA ashless dispersant as prepared in Example 1. The resulting lubricating oil possesses good dispersant and antirust properties.

#### Example 3

To 1000 parts of a solvent refined SAE-30 Pennsylvania base oil is added 10 parts of N,N-dimethyl-(3,5-di-tert-butyl-4-hydroxybenzyl)amine, 2.0 parts of calcium as calcium phenate having a base number of 210 and a molecular weight of 550 and 25 parts of a DEA dispersant as prepared in Example 1. The resulting oil possesses good dispersant and antirust properties.

#### Example 4

To 1000 parts of a Mid-Continent lubricating oil containing 0.1 part of zinc as zinc dithiophosphate and 5 parts of 4,4'-methylenebis(2,6-di-tert-butylphenol) is added 10 parts of calcium as an overbased calcium sulfonate having a base number of 200 and 100 parts of the DEA dispersant of Example 1. The resulting oil possesses good dispersant and antirust properties.

#### Example 5

To 1000 parts of solvent refined neutral oil having a 95 VI containing 6 percent of a commercial methacrylate type VI improver and 0.5 percent of 4,4'-methylenebis(2,6-di-tert-butylphenol) is added 0.1 part of calcium as an overbased calcium sulfonate having a base number of 300 and one part of the DEA type dispersant of Example 1.

#### Example 6

To 1000 parts of commercially available pentaerythritol ester having a viscosity of 100° F. of 22.4 centistokes, and known by the trade name "Hercoflex 600," is added one part of calcium as an overbased calcium phenate having a base number of 220 and a molecular weight of 600 and 10 parts of the DEA type dispersant of Example 1. The resulting synthetic oil possesses improved dispersant and antirust properties.

#### Example 7

To 1000 parts of dioctylsebacate having a viscosity at 210° F. of 36.7 SUS, a VI of 159, is added 0.5 part of calcium as an overbased calcium sulfonate having a base number of 350 and a molecular weight of 1000 and 30 parts of the DEA type dispersant of Example 1.

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## Example 8

A functional fluid is prepared from 1000 parts of a conventionally refined Pennsylvania mineral oil (99 SUS at 100° F.), 50 parts of a polymethacrylate having a molecular weight of about 7000, derived from a fatty alcohol, one part of a dimethyl silicone polymer anti-foam agent and 25 parts of a dialkyl zinc dithiophosphate, to which is added one part of calcium as an overbased calcium sulfonate having a base number of 300 and 25 parts of the DEA type dispersant of Example 1.

The antirust-dispersant combinations as made are very viscous. For this reason, they are preferably diluted with an oil of a type similar to that in which they will eventually be used. By way of example, the following illustrates some typical antirust-dispersant concentrates intended for use in automotive lubricating oil.

## Example 9

To 1000 parts of a SAE-20 solvent refined neutral oil is added 1000 parts of the DEA dispersant of Example 1 and 1.0 part of calcium as an overbased calcium sulfonate having a base number of 300 and a molecular weight of 940.

## Example 10

To 10,000 parts of a SAE-10 solvent refined neutral lubricating oil is added 500 parts of the DEA dispersant of Example 1 and 1000 parts of calcium as an overbased calcium phenate having a base number of 25 and a molecular weight of 600.

## Example 11

To 1000 parts of a SAE-20 solvent refined neutral lubricating oil is added 1000 parts of the DEA dispersant of Example 1 and 85 parts of calcium as an overbased calcium sulfonate having a base number of 300 and a molecular weight of 940. The overbased calcium sulfonate is added as a 30 percent solution in a hydrocarbon mineral oil.

The unusual properties of the DEA dispersants used in the compositions of this invention greatly increase the antirust properties obtained from oil soluble calcium compounds when compared with the antirust properties obtained from the same oil soluble calcium compound using a conventional amide type dispersant, as shown by the following tests. In these tests, the amide type dispersant is the reaction product of an alkenyl succinic anhydride (wherein the alkenyl group has a molecular weight of about 1000) with N,N-dimethyl-1,3-propanediamine.

The test used was the CLR Engine Rust Test. The test consists of 12 hours of operation at low temperature with some of the blowby products condensed and returned to the crankcase, which is followed by an 8 hour shutdown period. This cycle is run twice and the test is then completed with 2 hours of operation at high temperature, so that the test occupies a total elapsed time of 42 hours. Oil compositions are evaluated on the basis of the quantity of rust on the valve lifters and the polished push rods. A rating of 0 indicates the parts are fully coated with rust, and a rating of 10 indicates no sign of rust. Intermediate degrees of rust are shown by the numbers between 0 and 10. Test condition for the CLR Engine Rust Test are given in the following table.

TEST CONDITIONS FOR CLR ENGINE RUST TEST

	Low Temp.	Engine Off	High Temp.
Cycling Time, hr.....	12	8	2
Engine Speed, r.p.m.....	1,800	-----	2,500
Engine Load, percent WOT.....	50	-----	100
Coolant Out, ° F.....	85	85	195
Condenser Coolant, ° F.....	45	45	Off
Oil Gallery, ° F.....	120	-----	200
Intake Air Humidity, gr./lb. air.....	80	-----	80
Blowby, c.f.h.....	16	-----	( <sup>1</sup> )

<sup>1</sup> Not controlled.

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In the above table, percent WOT represents percent of wide open throttle.

The oil used in this test is a SAE 10W-30 lubricating oil derived from a typical solvent refined Mid-Continent neutral lubricating base oil containing a VI improver and 0.08 percent zinc as zinc dithiophosphate. The rust rating of this oil was 3.5 after only one cycle in the CLR Engine Rust Test. The test was not run for two cycles because of the probability of engine failure due to excessive rust. The rust rating of this oil was not improved by the addition of either the amide type dispersant or the DEA type dispersant.

Rust data comparing the effect of the DEA dispersant with the effect of the conventional amide type dispersant on the rust inhibiting properties of an overbased calcium sulfonate are shown in the following table at three different concentrations of the calcium sulfate.

COMPARISON OF THE EFFECT OF AMIDE TYPE DISPERSANT AND DEA TYPE DISPERSANT ON THE ANTI-RUST PROPERTIES OF CALCIUM SULFONATE

Dispersant (5 wt. percent)	Concentration of Ca sulfonate <sup>1</sup> (wt. percent Ca)		
	0.07	0.1	0.15
Amide Type.....	2.7	3.4	6.5
DEA Type.....	6.0	7.0	9.7
Improvement Factor.....	2.2	2.0	<sup>2</sup> 1.5

<sup>1</sup> Hybase C-300, product of Bryton Chemical Company, New York, N.Y.

<sup>2</sup> The decrease in improvement factor of high concentrations of Ca sulfonate is due to the fact that the DEA type is so close to 10 that it is running out of scale in the test.

As the above results show, the effect of calcium sulfonate as a rust inhibitor is unexpectedly doubled by the use of the DEA type dispersant. Another way to view this is that to obtain a rust rating of 6.0 using a DEA type dispersant requires only 0.07 weight percent calcium, whereas to obtain the same rust rating using a commercial amide type dispersant requires about twice as much calcium. This unexpected antirust bonus is obtained without loss of dispersancy as the DEA type dispersants of this invention are equal to the amide type in dispersancy effect.

Having fully described new lubricating oil compositions, it is intended that this invention should only be limited within the spirit and scope of the following claims.

We claim:

1. A composition consisting essentially of

(A) from about 10 to 99 weight percent of the reaction product of

(1) a mole of an alkenyl compound selected from the group consisting of alkenyl succinic acids and alkenyl succinic anhydrides having an alkenyl group having a molecular weight of from 700 to 1600, and

(2) from about 0.75 to 1.2 moles of diethanol amine at a temperature of from about 140 to about 180° C.

(B) from about 1 to 50 weight percent of an overbased calcium sulfonate selected from the group consisting of calcium phenates and calcium sulfonates.

2. The composition of claim 1 wherein said alkenyl compound is an alkenyl succinic anhydride wherein the alkenyl group is derived from a polybutene having a molecular weight of from about 700 to 1600.

3. The composition of claim 2 wherein said alkenyl group is a polybutenyl group having a molecular weight of from about 900 to 1100.

4. A lubricating oil composition containing the composition of claim 1 such that said lubricating oil contains from about 0.1 to 10 weight percent of said reaction product of an alkenyl compound and diethanol amine and from about 0.01 to 1 percent of said overbased calcium sulfonate.

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5. The composition of claim 4 wherein said alkenyl compound is an alkenyl succinic anhydride wherein the alkenyl group is a polybutenyl group having a molecular weight of from 700 to 1600.

6. The composition of claim 5 wherein said alkenyl group is a polybutenyl group having a molecular weight of from about 900 to 1100.

## References Cited

## UNITED STATES PATENTS

3,219,666 11/1965 Norman et al. ---- 252—51.5 X

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3,272,743	9/1966	Norman et al. -----	252—32.5
2,616,924	11/1952	Asseff et al. -----	252—33 X
2,839,470	6/1958	Warren et al. -----	252—33
3,324,033	6/1967	Knapp -----	252—51.5

## FOREIGN PATENTS

984,409 2/1965 Great Britain.

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