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3,791,971

LUBRICATING OIL COMPOSITIONS

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U.S. Cl. 252—33.4

8 Claims

ABSTRACT OF THE DISCLOSURE

Polyoxyalkylene glycols and their reaction products with organic diisocyanate and dicarboxylic acid are combined with alkaline earth metal carbonates dispersed in a hydrocarbon medium to provide lubricating compositions of superior acid neutralization capability and rust inhibition in internal combustion engines.

CROSS-REFERENCES

This is a continuation-in-part of copending application Ser. No. 142,838, filed May 10, 1971, which is itself a continuation-in-part of application Ser. No. 45,567, filed June 11, 1970, now Pat. No. 3,711,406.

BACKGROUND OF THE INVENTION

Field of the invention

Lubricating oils are employed as a vehicle for additives which promote the protection of the surfaces lubricated by the oil. The tendency for rusting in internal combustion engines requires that lubricating oils include additives which inhibit rust. The oxidation of lubricating hydrocarbon oils yields a variety of compounds that are deleterious for the service for which the oils are intended. A variety of end products result from this oxidation which attack metals, corrode bearings, and promote wear and rust. Acidic products are also a major source of the oil insolubles that cause ring sticking, sludging, and impede oil flow. The three important mechanisms available for inhibiting rust and corrosion are acid neutralization, inhibition of oil oxidation and protective film formation. Since acids are involved in the rust and corrosive processes, their neutralization will serve as a preventative. This function is performed by including in lubricating oils for internal combustion engines bases which are capable of neutralizing the acids formed during fuel combustion or introduced into the oil by blow-by or other mechanisms. For example, alkaline earth metal carbonates, when dispersed in a lubricating oil by means of a dispersant (phenate or sulfonate) will maintain low copper-lead bearing corrosion rates and inhibit rusting as long as the pH of the oil is above 6.

Rusting and acidic corrosion constitute serious problems in internal combustion engines, diesel engines, steam turbines, and other machinery exposed to moisture. Corrosive wear and rusting can be readily controlled by rapid neutralization of acids by effective alkaline additives.

DESCRIPTION OF THE PRIOR ART

Neutralization rate accelerators are new in the lubrication art. Polyoxyalkylene glycols and their esters have often been utilized as synthetic lubricants. Low molecular weight polyoxyalkylene glycols and their esters have found some use as lubricating oil additives. For example, U.S. Pat. 3,509,052 teaches the use of polyoxyalkylene polyols as demulsifiers in certain lubricating oil compositions.

SUMMARY OF THE INVENTION

The compositions of this invention are a combination of a polyoxyalkylene glycol; or a polyoxyalkylene glycol

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which has been capped with a polar functional group such as an amino amide, acid, ester, carbonyl, thio or phosphorus group; or the reaction product of a polyoxyalkylene glycol with a carboxylic acid or acid generating compound such as an acid halide or anhydride, or an organic isocyanate, and an alkaline earth metal carbonate dispersed in an oil of lubricating viscosity. The presence of a polyoxyalkylene glycol, or its derivatives, in the composition promotes the neutralization of acid from an aqueous phase mixed with the oil as determined by pH measurements. The compositions provide rust and corrosion protection.

DETAILED DESCRIPTION OF THE INVENTION

The combination of polyoxyalkylene glycols or their derivatives and alkaline earth metal carbonates dispersed in an oil of lubricating viscosity, in accordance with the present invention, results in surprising improvement in the rate of acid neutralization as demonstrated by the Acid Neutralization Rate Test to be described. This use of polyoxyalkylene glycols or their derivatives in combination with the dispersed carbonate inhibits rust formation and the corrosion of ferrous metal surfaces in contact with lubricants containing said combinations. The polyoxyalkylene glycols or their derivatives are present in amounts from 0.01 to about 5 percent by weight of the composition.

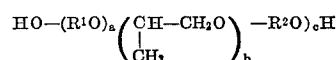
The alkaline earth metal carbonate will normally be present to provide alkalinity values of from about 0.5 to 100 mg. KOH/g., and more usually from about 1 to 20 mg. KOH/g. While alkalinity values in excess of 10 mg. KOH/g. are not essential for rusting protection, these values will frequently be used for a particular service. For example, in marine lubrication, alkalinity values are high, while in automobile lubrication, alkalinity values are relatively low.

Other additives may be present in the lubricating oil composition to fulfill functions other than those provided for by the dispersed carbonate base and the polyoxyalkylene glycol or its derivatives, as well as to augment the functions of the latter additives.

COMPONENTS

Polyoxyalkylene glycols

The polyoxyalkylene glycols which find use within the scope of the present invention consist of an oxalkane chain capped by hydroxyl groups and are of the general formula



wherein R¹ and R² are ethylene or propylene radicals a is in the range from 0 to b/5, b is in the range from 10 to 200, and c is in the range from 0 to b/5, such that the total molecular weight of the polyoxyalkylene glycol is in excess of 1,000.

Some of the lower molecular weight polyoxyalkylene glycols within this range, are commercially available from Wyandotte Chemicals Corporation as the Pluronic series. The block copolymers are prepared by adding propylene oxide to the two hydroxyl groups of a propylene glycol nucleus. The resulting hydrophobic base can be made to any controlled length varying from 800 to thousands in molecular weight. By adding ethylene oxide to both ends of this hydrophobic base, it is possible to put polyoxyethylene hydrophilic groups on both ends of the molecule. The hydrophilic groups may be added to constitute anywhere from a few percent to 80 percent of the final molecule, U.S. Pat. 2,674,619. In general, the polyoxyalkylene glycols are mixtures of compounds that differ slightly in the polymer chain length. However, their properties approximate those of the molecule represented by their average composition.

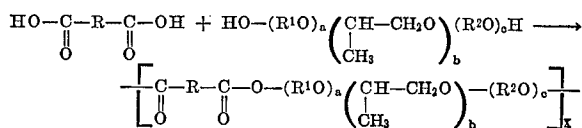
The overall structure of the preferred molecules of this invention is purposely amphipathic. An amphipathic molecule is an organic species encompassing in the same molecule two dissimilar structural groups, e.g., a water-soluble and a water-insoluble moiety. The composition, solubility properties, relation and relative sizes of these dissimilar moieties in relation to the overall molecular configuration determines the efficiency of the polyoxyalkylene glycol and its derivatives for our purposes. That is, as will be shown, the ability of the polyoxyalkylene glycol or its derivatives to accelerate the rate of neutralization of acid from an acidic phase by dispersed alkaline earth metal carbonate, depends on the total molecular weight and composition of the polyoxyalkylene glycol or its derivatives. This sensitivity to composition and amphipathic balance of the polyoxyalkylene glycol and their derivatives, may be related to our study of the rate of acid-base neutralization between an aqueous and nonaqueous phase which is archetypical of practical operating conditions in motors, engines and turbines.

Polyoxyalkylene glycol derivatives

Preferred neutralization accelerating derivatives of the polyoxyalkylene glycols have been produced by reacting the glycol with organic mono- and polyisocyanates; or mono- and dicarboxylic acids, or acid halides and anhydrides, all of which are defined as carboxylic generating compounds, to yield high molecular weight complex reaction products which may be typified as complex polyesters or urethanes. Other derivatives of polyoxyalkylene compounds which are useful to a lesser extent as neutralization rate accelerators when used in combination with dispersed alkaline earth metal carbonates include oxalkane chains capped with polar functional groups such as carbonyl, acidic, ester, amines, amides, thio and phosphoro groups, for example, see Lowe U.S. Pat. 3,037,056 and U.S. Pat. 8,879,230. Of these, the acetate ester-capped polyoxyalkylene glycols are preferred in many instances because of their solubility.

The dicarboxylic acids which can be utilized by reaction with polyoxyalkylene glycols include oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, and other α,ω -dicarboxylic acids and alkyl or alkenyl substituted acids of the same name. Of these, oxalic acid and its derivatives is especially preferred because of their stability and reactivity. In general, lower molecular weight acids such as acetic and oxalic are preferred over higher molecular weight acids such as substituted succinic acid, lauric, stearic and other fatty acids, because of the greater ease of reaction of the lower molecular weight acids and the stability and solubility of their polyoxyalkylene glycol esters.

The reaction between the high molecular weight polyoxyalkylene glycols and a dicarboxylic acid generating compound is carried out by mixing them directly, or solubilizing in a mutual solvent, in a mole ratio of from 1:3 to 3:1 and heating to about 150–200° C. for 1 to 100 hours. Suitable and well-known esterification catalysts may be utilized to shorten the time of the reaction. The reaction product is believed to be a complex ester of the following repeating unit.

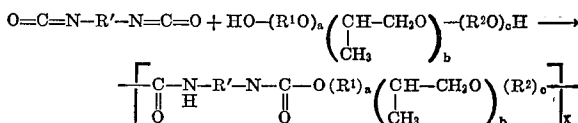


R is the substantially hydrocarbyl or substituted hydrocarbyl moiety of the dicarboxylic acid and R¹, R², a, b, and c have been previously defined. The number of repeating units is indicated by x and may range from about 1 to about 10 with the total molecular weight of the complex ester in the range from 1000 to about 50,000.

The organic isocyanates which can be utilized by reaction with polyoxyalkylene glycols include, for example,

phenyl isocyanate, toluene diisocyanate, methylene diphenyl diisocyanate, alkylated methylene diphenyl diisocyanate, hexamethylene diisocyanate, and polymeric isocyanates, such as polymethylene polyphenyl isocyanate.

The reaction between the high molecular weight polyoxyalkylene glycol and the organic isocyanate is carried out by directly mixing the reagents, or solubilizing in a mutual solvent, in a mole ratio of from 1:3 to 3:1 and heating to about 25–100° C. for from 3 to 48 hours. The urethanes which are produced by the reaction are believed to be typified by the following reaction scheme for the case of a diisocyanate



where R' is the substantially hydrocarbyl or hydrocarbyl substituted moiety of the diisocyanate, and R¹, R², a, b, and c have been previously defined. The number of repeating units is represented by x which may range from 1 to 10 and the resulting urethane has a total molecular weight in the range from about 1,000 to about 50,000.

To prepare the reaction product of polyoxyalkylene glycol and oxalic acid, 889 grams of the polyoxyalkylene glycol of Example 2 was mixed in a 3-liter flask with 250 ml. of xylene and 12.6 grams of oxalic acid dihydrate. The mixture was stirred and refluxed for 42 hours at temperatures in excess of 300° F. The product was stripped to 230° F. under vacuum. 890 grams of product was obtained, having an acid number of virtually zero. The reaction product of polyoxyalkylene glycol and toluene diisocyanate was prepared by mixing 111 grams of the polyoxyalkylene glycol of Example 2 with 4.35 grams of toluene diisocyanate in a 200-ml. flask. The reaction mixture was stirred for 15 hours at 205±5° F. The product was stripped to 200° F. under vacuum. 114 grams of product were obtained.

Alkaline earth metal carbonates

The alkaline earth metal carbonates are magnesium, calcium and barium carbonates, preferably calcium and barium carbonates. Small amounts of the hydroxides of the metals may be present, usually not contributing more than about 20 percent of the alkalinity value from the alkaline earth metal carbonate composition. The alkaline earth metal compounds are not soluble in hydrocarbon media, therefore they are invariably dispersed with some type of metal salt dispersant. These dispersants are well known in the art and will be discussed only summarily.

The preferred dispersants are sulfonate and phenate dispersants. The sulfonates are extensively discussed in U.S. Pat. No. 3,488,284. The organic sulfonates are prepared either from natural or synthetic sources. The natural sulfonates are referred to as mahogany sulfonates and are derived from petroleum mineral oil fractions, and normally have from about 25 to 50 carbon atoms per sulfonic acid. Synthetic sources are also employed which are usually alkylated benzenes having from about 25 to 50 carbon atoms. The use of the sulfonates and the method of preparing overbased sulfonates is well known and indicated in the above patent. Other relevant patents include U.S. Pat. Nos. 3,021,280, 3,256,186, 3,057,896 and 3,312,618.

Another class of dispersant for alkaline earth metal carbonates are the phenates. The phenates are alkylated phenols either individually or polymerized to a low order of from 8 to 5 alkyl phenols, normally bridged with sulfur, alkylene groups, or dialkylene amino groups (Mannich bases). The alkyl group on the phenol is normally of at least 8 carbon atoms and usually does not exceed 36 carbon atoms, more usually being in the range of about 12–30 carbon atoms. The phenoxide in the phenate also contributes to the alkalinity value. The overbased

phenates are described in numerous patents such as U.S. Pat. Nos. 3,474,035, 3,429,812, 3,388,063, 3,336,224, and 2,798,852.

Other dispersants which are employed are the alkaline earth metal alkylphosphonates and thiophosphonates. The phosphonates will normally contain at least about 30 carbon atoms and may contain as many as 200 carbon atoms, more usually from about 50–125 carbon atoms. These overbased phosphonates are described in U.S. Pat. No. 3,312,618.

The alkalinity value of the overbased dispersants will usually be at least 150 and not exceed 500, more usually being in the range of from about 200 to 450 mg. KOH/g. The equivalent ratio of base to dispersant will be at least 1:1 and more usually at least 1.5:1, normally not exceeding about 20:1.

These compositions are used in a sufficient amount to provide the desired alkalinity value in the final composition. Therefore, the alkaline earth metal carbonates are prepared as concentrates and then diluted in the lubricating oil medium, and the polyoxyalkylated compound is added to provide the desired end composition.

Lubricating oils

The oils which find use in this invention are oils of lubricating viscosity derived from petroleum or synthetic sources. The oils may be paraffinic, naphthenic, halo-substituted hydrocarbons, asphaltic, or combinations thereof. Synthetic lubricating oils include hydrocarbon oils and polymerized and interpolymerized olefins, alkylbenzenes, polyphenyls, alkylene oxide polymers and interpolymers, and derivatives thereof such as esters, ethers, etc. Silicone-based oils also form a useful class of synthetic lubricants.

Oils of lubricating viscosity normally have viscosities in the range of from 35–50,000 Saybolt Universal Seconds (SUS) at 100° F., more usually from about 50–10,000 SUS at 100° F.

Other additives

Other additives are often desirably included in the composition. These additives are pour point depressants, oiliness agents, anti-oxidants, detergents, corrosion inhibitors, extreme pressure agents, antifoamants, etc. Usually, for oils to be used in an engine the total amount of these additives will range from about 0.5–15 weight percent, more usually from about 0.5–10 weight percent. The individual additives may vary in amounts from about 0.01–10 weight percent of the total composition. In concentrates, the weight percent of these additives will usually range from about 0.3–30 weight percent.

A preferred group of additives is the succinimides of alkylene polyamines. The succinimides are useful as sludge dispersants. They usually have an alkyl or alkenyl bonded to the succinimide group of at least 50 carbon atoms and not more than about 200 carbon atoms. The alkylene polyamines are normally ethylene or propylene polyamines having from 2–6 amino groups, and more usually from about 3–5 amino groups; see, for example, U.S. Pat. 3,361,673.

An especially preferred group of additives, because of their effectiveness when used in combination with the neutralization rate accelerating compounds of this invention and dispersed alkaline earth metal carbonate, are the hydrocarbyl substituted amines and polyamines, for example, U.S. Pat. 3,565,804.

Another preferred aspect of using the compositions of this invention is the inclusion in the lubricating oil of from about 1 to 50 mm./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups contain from about 4–36 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. The remaining valence of the phosphorodithioate will usually be satisfied by zinc, but polyoxyalkylene or a third hydrocarbyl group may also be used.

Neutralization rate test

The Neutralization Rate Test (NRT) consists of the neutralization of an acidic aqueous phase with a basic oil phase. The progress of the neutralization is followed with a pH meter by measuring the pH at 15-sec., or some other convenient interval. The pH is then plotted versus the time. Lubricating oil compositions containing dispersed alkaline earth metal carbonates will neutralize the acid and exhibit a definite point of inflection (PI), usually in the pH range of 3.5–6.5, but the time elapsed to the point of inflection (TPI) varies widely depending on the presence or absence of a neutralizing rate accelerator of the present invention, all other test factors being kept constant.

It is believed that the PI corresponds to the first end point for the acid-base titration in the given system. For example, the first end point in the purely aqueous titration of 0.01 N HCl with 0.02 N sodium carbonate occurs at pH 4.5 and is believed to correspond to the conversion of HCl to carbonic acid. A second end point occurs at pH 8.1 and is believed to correspond to the conversion of dissolved carbonic acid to bicarbonate.

The time elapsed from initial mixing of oil and aqueous phase to the PI is the TPI and it forms the basis for comparing various oil compositions in the NRT. In general, in the comparison of two oil compositions, the one with a low TPI rating (fast acid neutralization) has appeared to have better rust performance than the composition with higher TPI (slower acid neutralization) all other factors being kept constant. In examples to be elaborated below, the performance of the lubricating oil compositions in the well-known Sequence IIB engine test are related to NRT results in these cases, all other factors being kept constant.

Thus, the NRT is used to test the efficiency of the polyoxyalkylene glycols and their derivatives as oil-soluble neutralization rate accelerators. Test procedure is as follows: A 250-ml. beaker containing aqueous HCl (0.01–0.003 N) is fitted into a test stand with a stirring paddle and the electrodes of a Beckman Expandomatic pH meter immersed in the solution. For highest reproducibility, the rate of stirring (500 r.p.m.) should be constant and the electrodes (Calomel and Glass electrodes) should be in the same relative position for each test. Since the oil phase may have a tendency to foul the Glass electrode, periodic application of Desicote (Beckman hydrophobic surface coating) should be applied as a preventative. Next, the test oil composition, 50 ml., is layered onto the aqueous with as little mixing as possible. The pH meter, stopwatch, and the stirrer are started simultaneously. pH readings are then made at known elapsed times and plotted versus the time. The TPI will vary from more than 150 minutes for certain tested oil compositions containing carbonate, but having no acid neutralization rate accelerators, to less than 1 minute with certain polyoxyalkylene glycols or their derivatives.

Important test parameters are, first, base oil viscosity which should not vary by more than 15 percent in any comparison of lubricating oil compositions; secondly, the normality of the acid which, if reduced by one-half reduces the TPI (roughly) by one-half. This parameter may be used to adjust the scale of neutralization times in different series of tests. Reproducibility of the NRT has been established by extensive testing.

EXAMPLES

The following examples are illustrative of the improved lubricating oil compositions of the present invention utilizing alkaline earth metal carbonates and neutralization rate accelerators as described heretofore. All percentages are in weight percent of the total composition unless otherwise noted.

Example 1

A lubricating oil composition consisting of a neutral petroleum oil of viscosity 100 SUS at 100° F., 25 mM./

kg. of a calcium carbonate sulfonate-dispersant composition containing 2.35 percent calcium, 40 mM./kg. of a calcium carbonate phenate-dispersant composition containing 9.25 percent calcium, 25 mM./kg. of zinc dithiophosphate composition containing 2.85 percent phosphorus and 4 percent by weight of polyisobutylene succinimide of tetraethylene pentamine (mole ratio of succinic anhydride to polyamine 0.50).

Example 2

The lubricating oil composition of Example 1 with the addition of 0.1 percent of polyoxyalkylene glycol block copolymer having about 10 percent by weight of polyoxyethylene and 90 percent by weight of polyoxypropylene, and molecular weight of about 4,440.

Example 3

Lubricating oil composition of Example 1 with the addition of 0.05 percent or more of the reaction product of the polyoxyalkylene glycol of Example 2 with toluene diisocyanate in a mole ratio of approximately 1:1.

Example 4

A lubricating oil composition consisting of a neutral petroleum oil of viscosity 100 SUS at 100° F., 25 mM./kg. of a calcium carbonate sulfonate-dispersant composition containing 2.35 percent calcium, 40 mM./kg. of a calcium carbonate phenate-dispersant composition containing 9.25 percent calcium, 15 mM./kg. of zinc dithiophosphate composition containing 2.85 percent phosphorus and 4 percent by weight of polyisobutylene succinimide of triethylene tetramine.

Example 5

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the polyoxyalkylene glycol block copolymer of Example 2.

Example 6

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with oxalic acid in the mole ratio of 2:1.

Example 7

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyalkylene glycol of Example 2 with oxalyl chloride in the mole ratio of 1:1.

Example 8

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with toluene diisocyanate in the mole ratio 1:1.

Example 9

The lubricating oil composition of Example 8 wherein the toluene diisocyanate and the polyoxyalkylene glycol are reacted in the mole ratio of 1:2.

Example 10

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with polyisobutenyl succinic anhydride in the mole ratio of 1:2.

Example 11

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with dodecenyl succinic anhydride in the mole ratio of 1:2.

Example 12

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the poly-

oxyalkylene glycol of Example 2 with sebacic acid in the mole ratio 1:1.

Example 13

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with phenyl isocyanate in the mole ratio of 1:2.

Example 14

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with acetic acid in the mole ratio 1:2.

Example 15

The lubricating oil composition of Example 4 with the addition of 0.1 percent of the reaction product of the polyoxyalkylene glycol of Example 2 with decanoic acid in the mole ratio 1:2.

TABLE I

Composition ¹	Percent additive ²	TPI ³
1.....	0	>300
2.....	0.1	2
3.....	0.05-0.5	1-16
4.....	0	>300
5.....	0.1	2.5
6.....	0.1	1.0
7.....	0.1	3
8.....	0.1	0.33
9.....	0.1	0.83
10.....	0.2	16
11.....	0.1	2-6
12.....	0.1	2
13.....	0.1	13
14.....	0.1	3
15.....	0.1	15

¹ Compositions correspond to numbered examples of the same number.

² Weight percent of neutralization rate accelerator in lubricating oil composition containing dispersed alkaline earth metal carbonate.

³ Time to point of inflection (TPI) in minutes, 0.01 N HCl aqueous phase in the neutralization rate test.

TABLE II

Composition ¹	Percent polyoxyethylene ²	Percent polyoxyalkylene glycol ³	Molecular weight ⁴	TIP ⁵
A.....	0	0	-----	165
	0	0	-----	326
B.....	10	0.2	4,440	<1
	10	0.1	4,440	1-2
	10	0.2	3,610	<1
	10	0.1	3,610	3
A.....	10	0.5	2,500	1
	10	0.5	2,500	<1
	10	0.2	2,500	3
B.....	10	0.1	2,500	>30
	10	0.5	1,940	<1
	10	0.2	1,940	>30
A.....	10	0.5	1,050	2
B.....	10	0.5	1,050	56
	30	0.5	2,500	37
A.....	30	0.5	1,700	2
	50	0.5	1,900	>40
	50	0.5	4,500	>40
	<10	0.1	6,500	1.0
	<10	0.075	6,500	4.6
B.....	<10	0.05	6,500	73
	0	0.05	8,000	1.65
	0	0.025	8,000	6.25

¹ Composition consisting of reference oils A or B including dispersed alkaline earth metal carbonate and polyoxyalkylene glycol as shown, in indicated percentages. Reference Oil A is a neutral petroleum oil of viscosity 120 SUS at 100° F., 80 mM./kg. of zinc dithiophosphate and 2 percent by weight of polyisobutenyl succinimide of tetra ethylenepentamine. Reference oil B is a neutral petroleum oil of viscosity 100 SUS at 100° F., 25 mM./kg. of calcium carbonate sulfonate dispersant composition containing 2.35 percent calcium, 40 mM./kg. of calcium carbonate-phenate dispersant composition containing 9.25 percent calcium, 15 mM./kg. of zinc dithiophosphate and 4 percent by weight of polyisobutenyl succinimide of triethylene tetramine.

² Percent by weight of polyoxyethylene in polyoxyalkylene block copolymer, remainder is polyoxypropylene.

³ Percent by weight of polyoxyalkylene glycol in composition.

⁴ Average molecular weight of polyoxyalkylene glycol.

⁵ Time to point of inflection (TPI) in minutes, 0.01 N HCl in aqueous phase in neutralization rate test.

Table I illustrates the remarkable reduction in neutralization times achieved by the addition of even very small percentages of neutralization rate accelerators. Neutralization times for the reference oils containing calcium carbonate dispersed by sulfonates and phenates is exces-

sive, in spite of the fact that the oils have high alkalinity. The neutralization rate accelerators illustrated in Table I exemplify satisfactorily performing neutralization promoters. In general, neutralization rate accelerators which substantially reduce the TPI relative to that of the reference oil (zero-weight percent of acid neutralization accelerator) are preferred, since reduction in the TPI of better than 50 percent is regarded as evidence that the addition agent will function to help fulfill the objects of this invention. There are, of course, other properties which are needed such as additive compatibility, stability, etc. So far as rust inhibition is concerned, there is strong evidence that while a satisfactory NRT result is not quantitatively predictive of an MS Sequence IIB rust rating, at the very least, the NRT result does tend to correlate with the comparative rust inhibition properties of any two additives, all other factors being kept constant.

Table II illustrates the distinguishing characteristics of the polyoxyalkylene glycols of the present invention. It is clear that preferably the polyoxyalkylene glycol should contain substantially less than 50 percent polyoxyethylene units by weight and should have a molecular weight substantially over 1,000 and preferably substantially over 5,000.

TABLE III

Composition ¹	Percent additive ²	AER ³
C-----	0	6.5-7.4
	0.1	9.2
D-----	0	7.1-8.5
	0.1	9.0
E-----	0	8.9
	0.1	7.9
F-----	0	9.0
	0.1	9.0

¹ Lubricating oil compositions containing at least 25mM/kg. of calcium carbonate-sulfonate dispersant composition containing 2.35 percent calcium (C, D, E), at least 25 mM/kg. of calcium carbonatephenate dispersant composition containing 9.25 percent calcium, 15 mM/kg. of zincdithiophosphate, at least 4 percent by weight of polyisobutenyl succinimide of triethylene tetramine (C, D), 3 percent by weight of polyisobutenyl succinimide of tetra ethylene pentamine (E) and 3.3% by weight of polyisobutenyl amine (F).

² Percent of polyoxyalkylene glycol neutralization rate accelerator of Example 2 added to lubricating oil composition.

³ A average engine rust in the sequence IIB engine test.

Other test results show, for example, that the lubricating oil composition of Example 2 gives a satisfactorily clean diesel engine after several hours of running, and also gives a rust rating of 9.2 in the MS Sequence IIB engine rust test (GM specifications require an average engine rust rating of 8.9 to pass the MS Sequence IIB test). Table III illustrates the excellent IIB Average Engine Rust ratings (AER) obtainable from the combination of dispersed alkaline earth metal carbonate and polyoxyalkylene glycol and its derivatives in a lubricating composition. The aforementioned table illustrates that the carbonate alone is insufficient to retard rust formation to the degree desired, although the absence of acid neutralizing carbonate would, of course, lead to severe corrosion and rusting.

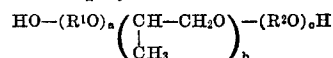
Finally, the use of the compositions of polyoxyalkylene glycols and their derivatives permits smaller amounts of ash to be introduced into the lubricating oil and therefore avoids problems associated with high ash oils.

What is claimed is:

1. A lubricating oil composition comprising:

a major amount of a hydrocarbon oil of lubricating viscosity;

from about 0.01 to 5 weight percent of at least one oil-soluble acid neutralization accelerating amphipathic block copolymer of the formula



wherein R¹ and R² are ethylene or propylene radicals, a is in the range of 0 to b/5, b is in the range from 10 to 200, and c is in the range from 0 to b/5, such that the total molecular weight of said compound is in excess of 1,000;

and sufficient alkaline earth metal carbonate dispersed in said hydrocarbon oil, with a dispersant selected from the group consisting of phenates and sulfonates, to provide an alkalinity value of from 0.5 to 100 mg. KOH/g.

2. A lubricating oil composition comprising:

a major amount of a hydrocarbon oil of lubricating viscosity;

from about 0.01 to 5 weight percent of an amphipathic oil-soluble acid neutralization accelerating composition which is the reaction product of a polyoxyalkylene glycol having a molecular weight in the range from 1,000 to 10,000 with an organic isocyanate;

and sufficient alkaline earth metal carbonate dispersed in said hydrocarbon oil, with a dispersant selected from the group consisting of phenates and sulfonates, to provide an alkalinity value of from 0.5 to 100 mg. KOH/g.

3. A composition according to claim 1 wherein said alkaline earth metal carbonate is calcium carbonate.

4. A composition according to claim 3 wherein said dispersant is a sulfonate dispersant derived from a sulfonic acid of from 25 to 50 carbon atoms.

5. A composition according to claim 3 wherein said dispersant is a phenate derived from alkylated phenol or polymerized alkylated phenols having 2 to 5 phenol groups per molecule and an alkyl group of from 12 to 30 carbon atoms.

6. A composition according to claim 2 wherein said alkaline earth metal carbonate is calcium carbonate.

7. A composition according to claim 6 wherein said dispersant is a sulfonate dispersant derived from a sulfonic acid of from 25 to 50 carbon atoms.

8. A composition according to claim 6 wherein said dispersant is a phenate derived from alkylated phenol or polymerized alkylated phenols having 2 to 5 phenol groups per molecule and an alkyl group of from 12 to 30 carbon atoms.

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