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POLYOXYALKYLENE LUBRICANT COMPOSITION

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The present invention relates to the preparation of novel oleaginous compositions useful as lubricants. More particularly, the invention has to do with the preparation of lubricating oil compositions comprising, as essential ingredients, polymeric material of the polyoxyalkylene type and an organo silicon compound which is an ester of a silicic acid.

The problem of keeping abreast with the constantly changing and increasingly exacting lubrication requirements of engines constantly being developed, particularly aircraft and automotive, is a major one confronting the petroleum industry. For example, continued refinement of gas turbine engines, such as turbo-jets and turbo-props, depends to a great extent on the development of lubricants capable of satisfactorily lubricating the moving parts, such as bearings and gears, of these engines.

While heretofore lubricating oils based on mineral hydrocarbon oils have been modified to render them suitable for increasingly exacting uses by improved refining techniques and by the use of additives, such lubricating oils suffer from certain inherent disadvantages which limit the usefulness thereof.

Thus, lubricating oil compositions are constantly being sought which have improved viscosity-temperature relationships, that is, a low viscosity at low temperatures, for example, —65° F. and lower, to permit easy starting, and high viscosity at high temperatures, up to as high as 500° F., to retain lubricity and thus prevent scuffing of metal parts; improved stability against oxidative deterioration in high temperature operations; improved volatility characteristics so that at the higher temperature, loss of lubricant through vaporization is minimized; improved anti-wear properties when used with highly loaded bearings and gears, and improved anti-corrosion properties.

Accordingly, an object of the invention is to prepare lubricating oil compositions having improved viscosity-temperature characteristics.

Another object of the invention is to prepare lubricating oil compositions having improved volatility properties at high temperatures.

Still another object of the invention is to prepare lubricating oil compositions having superior anti-wear properties for highly loaded bearings and gears.

Yet another object of the invention is to prepare lubricating oil compositions having improved resistance toward oxidative deterioration.

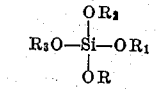
These and other objects and advantages of the invention will be apparent from the ensuing description of the invention.

Broadly, the invention is predicated on the discovery that a blend of polyalkylene glycol polymeric material and soluble therein an ester of a silicic acid in proportions, by volume, of about at least 20 per cent of either component, and the remainder, the other component, has superior viscosity-temperature properties, good volatility characteristics, unexpected anti-wear properties, and high stability toward oxidation and corrosion.

The amount in the blend of either component can range

from about one-fourth to four-fold the amount, by volume, of the other component, that is, 20 to 80 per cent, preferably 40 to 60 per cent, by volume, of either component. Often the organo silicon compound and polyalkylene glycol polymeric material are advantageously employed in equal amounts by volume.

The preferred esters contemplated by the invention are those of orthosilicic acid conforming to the formula

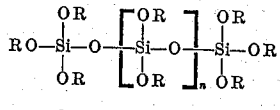


wherein R, R_1, R_2 and R_3 are like or different organic hydrocarbons, or equivalent, groups of 1, preferably at least 3, to about 18 carbon atoms, most advantageously 5 to 8 carbon atoms, such as alkyl, aryl, alkaryl, arylalkyl, alkoxyalkyl, alicyclic, saturated and unsaturated, for example, methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, butoxyethyl, vinyl, benzyl, xylyl, xenyl, allyl, butenyl, cyclohexyl, phenyl, etc.

In addition, those orthosilicates are preferred in which the carbon atoms in the organic portion of the molecule are of branched chain structure, such as those derived from secondary and tertiary alcohols or primary alcohols having alkyl substituents in the 2-position. It has been found that hydrolytic stability is greatest with tertiary carbon structure and decreases in the order of secondary carbon structure, followed by branched chain normal and then straight normal. Likewise, oxidative stability decreases in the order of tertiary, primary, and secondary carbon structures. Ideally, therefore, the orthosilicate selected will be one in which the carbon groupings will all be of tertiary carbon structure, and where this is not permitted, a maximum number of tertiary carbons, with the remainder being primary carbon chains.

Specific examples of orthosilicate esters contemplated by the invention are tetraethyl silicate, tetraisopropyl silicate, tetra (n-butyl) silicate, tetra (2,2-dimethyl propyl) silicate, tetra (2-butyl) silicate, tetra (2-pentyl) silicate, tetra (3-amyl) silicate, tetra (2-methyl-1-butyl) silicate, tetra (2-methyl-2-butyl) silicate, tetra (n-hexyl) silicate, tetra (2-hexyl) silicate, tetra (4-methyl-2-pentyl) silicate, tetra (2-ethyl-1-butyl) silicate, tetra (2-heptyl) silicate, tetra (2-octyl) silicate, tetra (2,4-dimethyl-3-pentyl) silicate, tetra (2-ethyl-1-hexyl) silicate, tetra (n-decyl) silicate, tetra (1-methoxyl-2-propyl) silicate, tetra (n-dodecyl) silicate, tetra (n-hexadecyl) silicate, tetra (n-octadecyl) silicate, tetra (1-butoxyl-2-propyl) silicate, bis (2-butyl) bis (2-ethyl-1-butyl) silicate, isopropyl-tris (2-pentyl) silicate, bis phenyl-bis (4-methyl-phenyl) silicate, tetra (4-methyl-phenyl) silicate, tetra (4-methyl-phenyl) silicate, tetraphenyl silicate, tetracyclohexyl silicate, tetra (4-vinyl-phenyl) silicate, tetra (2-butoxyethyl) silicate, tetra (2 - methoxyphenyl) silicate, and tetra (2 - cyclohexenyl) silicate.

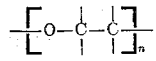
While the esters of orthosilicic acid are preferred in carrying out the invention, esters of other silicic acids can be employed in accordance with the invention. These may be represented by the formula



in which n is zero for esters of disilicic acid or at least 1 for the higher silicic acids, such as trisilicic acid. In general the R groups in the above formula are similar or dissimilar organic radicals of like definition given for the characterization of the orthosilicates, the preferred groups being of branched chain structure as already described in defining the orthosilicates.

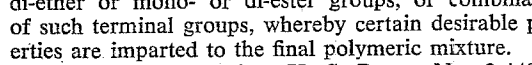
The preferred class of polyoxyalkylene polymeric ma-

terial, the other essential ingredient of the blend, is that having the polymeric structural configuration



These materials are prepared from the alkylene oxides, such as ethylene oxide, 1,2-propylene oxide, the 1,2-butylene oxides and higher homologs, and mixtures thereof, and the corresponding alkylene glycols. The resulting products may be polyoxyalkylene diols or polyalkylene glycol derivatives in which one or both of the terminal hydroxy groups have been removed either during the polymerization reaction or subsequently thereto, as by etherification or esterification, to yield mono- or di-ether or mono- or di-ester groups, or combinations of such terminal groups, whereby certain desirable properties are imparted to the final polymeric mixture.

By way of illustration, U. S. Patent No. 2,448,664 describes the preparation of a polyoxypropylene polymeric mixture according to the equation:



Monohydric alcohol	1,2-propylene oxide	Polyoxypropylene monohydroxy compound

As hereinabove indicated, the terminal hydroxyl group may be removed or capped by esterification or etherification to yield a mono-ether mono-ester or diether polypropylene glycol, respectively. Indeed, for purposes of the present invention, a polyalkylene glycol free of terminal hydroxyl groups, that is, one having either terminal ester and/or ether groups is preferred.

Polyoxyalkylene polymeric and copolymeric mixtures containing polymer units having more than two carbon atoms separating oxygen atoms have also been prepared and described. For example, U. S. Patent No. 2,520,733 describes the preparation of polymers and copolymers derived from trimethylene glycol.

The foregoing compounds, as well as additional polymeric materials contemplated by the invention, are further described in U. S. Patent No. 2,491,432. These compounds and materials range in molecular weight from about 400 to 2000 and higher. Most advantageously employed in accordance with the invention are monoether-monoester or diether derivatives of polyalkylene glycols having a molecular weight between about 400 and 800, preferably between about 400 and 600.

As hereinbefore indicated, the compositions prepared in accordance with the invention have certain properties, due to the conjoint presence of the two essential ingredients of polyalkylene glycol polymer and organo silicon compound which render them suitable for uses having most stringent requirements. To illustrate, it is desirable that a gas turbine lubricant have not to high a viscosity at low temperatures, that is, not more than 5000–10,000 centistokes at —65° F.; not too low a viscosity at the higher temperatures, that is, a minimum of about 3 centistokes at 210° F.; a minimum volatility, as measured by flask (Cleveland open cup), not below about 300° F., preferably not below 350–375° F.; a maximum pour of below —65° F., and, preferably, below —75° F.; a viscosity-temperature slope between 210° F. and —65° F. not exceeding about 0.75. Other properties are oxidative stability and anti-corrosion, good oiliness and ability to lubricate under extreme pressure conditions. Also desirable is good response to the addition of one or more additives to modify the properties of the compositions desirably.

A most important property of the composition prepared in accordance with the invention is their good wear characteristics. Indeed, the superiority of the present compositions in regard to wear is, as hereinbefore indicated, unexpected. Thus the compositions of the present invention have wear characteristics which are better than either ingredient taken alone. A convenient method of determining this property and the one utilized in obtaining the data appearing in the examples, is the well-known Falex wear test, described, for example, in the "Journal of the Institute of Petroleum," vol. 32, April 1946. In obtaining the data hereinbelow appearing, the following conditions were observed: Speed, 300 R. P. M.; load, 500 lbs.; time, 30 minutes; specimens, steel on steel. The weight of the shaft before and after the test was noted, the loss in weight in milligrams indicating the amount of wear.

Compositions of the present invention may have a wear rate of as low as 3 mg. weight loss; the order of wear of a typical high grade mineral oil is around 30 mg.

The tabulated data appearing below illustrate the unexpected wear superiority of the present compositions. These data were obtained employing the wear test hereinabove mentioned. The numerals appearing after "Tetra (2-ethylhexyl) silicate" and the polyalkylene glycol polymeric material, "Sec.-butyl methyl polypropylene glycol diether (m. w. about 600)" indicate amounts of each in volume per cent. The numerals appearing after "Wear" indicate weight loss in milligrams, two tests being performed for each column.

Tetra (2-ethylhexyl) silicate	100	80	60	40	0
Sec.-butyl methyl polypropylene glycol diether (m.w. about 600)	0	20	40	60	100
Wear	11.1, 9.6	3.1, 3.2	3.5, 3.9	1.6, 0.8	6.3, 6.1

The data indicate that whereas the silicate alone gave a weight loss of 11.1 and 9.6 mg. and the polyalkylene glycol polymeric material alone gave a weight loss of 6.3 and 6.1 mg., addition of 20 per cent or more of one to the other resulted in a substantial reduction of weight loss.

The following examples further illustrate compositions prepared in accordance with the invention.

Example 1

Polymeric material having a viscosity of 61.2 seconds Saybolt (SSU) at 210° F. and prepared from 1,2-propylene oxide and 2-ethylhexanol was mixed in equal amounts, by volume, with tetra (2-ethylhexyl) orthosilicate. Addition of 1% phenyl-α-naphthyl amine and 6% polymethacrylate viscosity index improver resulted in a composition suitable for turbo-prop lubrication.

The composition analyzed as follows:

Flash, Cleveland open cup, °F	360
Fire, °F	420
Viscosity, in centistokes:	
At 210° F	6.69
At 100° F	24.7
At —40° F	4300
Viscosity index	182
Viscosity temperature slope[1] (210° F. to —40° F.)	0.61
Pour point, °F	below —65° F.
Evaporation test, ASTM D–972–48T, 22 hours at 275° F., per cent weight loss	8.3
Falex wear test, mg. weight loss	3.0

[1] Utilizing ASTM Standard Viscosity-Temperature Chart E for Liquid Petroleum Products (D–341), the ratio of the linear distance between measured viscosities at —40° F. and 210° F. plotted on the ordinate, and the linear distance between temperatures of —40° F. and 210° F. measured along the abscissa.

Example 2

An n-butyl methyl polypropylene glycol diether having a molecular weight of about 500 was mixed with tetra (2-ethylhexyl) orthosilicate in amounts of 30 and 70 volume per cent, respectively. To the resulting blend there was added, by weight of the finished composition, 0.05 per cent mercaptobenzothiazole and 0.1 per cent 1,3,4-thiadiazolyl-2,5-bis(dialkyl dithiocarbamate). The

finished composition, suitable as a lubricant for turbo-jets and turbo-props, analyzed as follows:

Flash, Cleveland open cup, °F	380
Fire, °F	420
Viscosity, in centistokes:	
At 210° F	2.7
At 100° F	9.03
At —65° F	4800
Viscosity index	155
Pour point, °F	below —65° F.
Evaporation test, ASTM D–972–48T, 22 hours at 275° F., per cent weight loss	8
Falex wear test, mg. weight loss	4.3

Example 3

About 80 volume per cent hexa(2-ethyl-1-butoxy) disiloxane was mixed with about 20 volume per cent of n-butyl methyl polypropylene glycol diether. The composition analyzed as follows:

Flash, Cleveland open cup, °F	400
Fire, °F	450
Viscosity, in centistokes:	
At 210° F	3.01
At 100° F	8.71
At —65° F	863
Viscosity index	208
Pour point, °F	below —80° F.
Evaporation test, ASTM D–972–48T, 22 hours at 275° F., per cent weight loss	4.3
Falex wear test, mg. weight loss	4.0

Example 4

An n-butyl methyl diether copolymer of ethylene oxide-1,2-propylene oxide, in a mol ratio of 25 ethylene oxide to 75 mol per cent propylene oxide and having a molecular weight of about 500 was mixed in equal proportions by volume with 4-methyl-2-pentyl silicate. The resulting composition, useful as a gas turbine lubricant and hydraulic fluid, had the following properties:

Flash, Cleveland open cup, °F	350
Fire, °F	390
Viscosity, in centistokes:	
At 210° F	2.15
At 100° F	6.5
At —65° F	2800
Viscosity index	144
Pour point, °F	below —80° F.

Example 5

About 30 volume per cent of polytrimethylene glycol polymer (molecular weight, about 860) was mixed with about 70 volume percent of tetra (butoxyethyl) orthosilicate. To this mixture was added about 0.5% of phenothiazine and 0.1% of mercaptobenzathiazole. The finished composition was useful as a hydraulic transmission fluid. It analyzed as follows:

Flash, Cleveland open cup, °F	380
Viscosity, in centistokes:	
At 210° F	2.55
At 100° F	7.6
At —30° F	290
Viscosity index	178

Example 6

A useful composition for the lubrication of sensitive instruments requiring freely moving parts for accuracy, breech mechanisms and the like was made up by mixing about 10 volume per cent polypropylene glycol having a molecular weight of about 630 with about 90 volume

per cent tetra (¼ 2-propyl, ¾ 2-octyl) orthosilicate. The composition had the following properties:

Flash, °F	350
Viscosity, in centistokes:	
At 210° F	2.1
At 100° F	6.5
At —30° F	300
Viscosity index	134

Example 7

Polypropylene glycol mono isooctyl ether having a molecular weight of about 600 was mixed in equal proportions by volume with hexa (2-methylbutyl) disiloxane. The finished composition was useful as a hydraulic transmission fluid, gas compressor lubricant, or turbine oil. It analyzed as follows:

Flash, Cleveland open cup, °F	370
Viscosity, in centistokes:	
At 210° F	3.3
At 100° F	11.5
At —30° F	600
Viscosity index	177

As will occur to those skilled in the art, and as has hereinabove been indicated, the compositions of the present invention are useful as gas turbine lubricants, hydraulic fluids, instrument oils, turbine oils, transmission fluids, ice machine oils, and others. Those oils may be improved, moreover, by the presence of one or more inhibitors, and as oxidation and corrosion inhibitors, anti-wear agents, rust inhibitors, foam inhibitors, etc.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A lubricant composition comprising a dialkyl poly-1,2-propylene glycol diether having a molecular weight of from about 400 to 800 and wherein the alkyl end groups contain from 1 to 8 carbon atoms, together with an amount of from about one-fourth to about four-fold, in terms of the volume of said ether, of a member of the group consisting of tetraalkyl silicate and hexaalkoxy disiloxane wherein said alkyl groups contain from 5 to 8 carbon atoms each and have a branched-chain structure.

2. A lubricant composition comprising a dialkyl poly-1,2-propylene glycol diether having a molecular weight of from about 400 to 800 and wherein the alkyl end groups contain from 1 to 8 carbon atoms, together with an amount of from about one-fourth to about four-fold, in terms of the volume of said ether, of a tetraalkyl silicate wherein said alkyl groups contain from 5 to 8 carbon atoms and have a branched-chain structure.

3. A lubricant composition comprising a dialkyl poly-1,2-propylene glycol diether having a molecular weight of from about 400 to 800 and wherein the alkyl end groups contain from 1 to 8 carbon atoms, together with an amount of from about one-fourth to about four-fold, in terms of the volume of said ether, of a hexaalkoxy disiloxane wherein said alkoxy groups contain from 5 to 8 carbon atoms and have a branched-chain structure.

4. A lubricant composition comprising a sec.-butyl methyl polypropylene glycol diether having a molecular weight of from about 400 to 800 and from about one-fourth to about four-fold, in terms of the volume of said ether, of tetra(2-ethyl hexyl) silicate.

5. A lubricant composition comprising a di(2-ethyl hexyl) polypropylene glycol diether having a molecular weight of from about 400 to 800 and from about one-fourth to about four-fold, in terms of the volume of said ether, of tetra(2-methyl hexyl) silicate.

6. A lubricant composition comprising an n-butyl methyl polypropylene glycol diether having a molecular weight of from about 400 to 800 and from about one-fourth to about four-fold, in terms of the volume of said ether, of hexa(2-ethyl-1-butoxy)disiloxane.

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