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EMULSIFIABLE LUBRICANT COMPOSITIONS

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This invention is directed to lubricant compositions emulsifiable in water. The lubricating compositions of this invention are particularly suitable for the lubrication of large low-speed diesel engines.

For the purpose of keeping maintenance costs as low as possible, low-speed diesel engines have for many years used high-quality, relatively expensive fuels. In more recent years, attempts have been made to use a lower quality fuel, that is, a heavy fuel oil, particularly by the operators of diesel engines of the cross-head type used in marine service. Such lower quality fuels have high sulfur contents, for example, from 1% to 5%, by weight; and the sulfur in these fuels adds to the over-all formation of carbon deposits and acidic components, causing increase in wear.

More recently it has been discovered that high-sulfur fuels can be used in the operation of large, low-speed diesel engines if water-oil emulsion type lubricants are used for upper head cylinder lubrication. It is noticed that the use of emulsion type lubricants for such service results in a marked improvement in piston and cylinder cleanliness in addition to the considerable reduction in wear relative to that obtained with lubricants previously used in conjunction with high-sulfur fuels.

Water-oil emulsion lubricants of themselves are not new in the art of lubrication. For example, in addition to the above, water-oil emulsions are used for lubrication in metal working operations and in the lubrication of steam cylinders. A primary reason for the lack of acceptance of emulsion lubricants where such possibly could be used has been the difficulty of inhibiting the formation of rust and corrosion.

Difficulties have been encountered in the use of water-oil emulsions in lubrication of marine diesel engines. In cold climates, for example, the aqueous phase of the emulsions can become frozen, resulting in a composition which is not re-emulsifiable. Furthermore, when the marine emulsion lubricants are stored in engine rooms aboard ships, the high temperatures tend to make the emulsions unstable. Also, the presence of large quantities of water in the emulsion lubricants makes the transportation of these lubricants to the point of use (and subsequent storage) unnecessarily expensive.

In accordance with this invention, it has been discovered that a remarkably effective water-emulsifiable lubricant useful for upper cylinder lubrication in diesel engines is obtained by the formation of a composition comprising a major proportion of an oil of lubricating viscosity, and minor proportions of an oil-soluble, divalent metal sulfonate, an oil-soluble divalent metal phenate, and a water-soluble divalent metal salt of an organic acid. Such a water-emulsifiable lubricant is obtained by substantial removal of the water phase from a water-in-oil emulsion comprising water, an oil of lubricating viscosity, an oil-soluble divalent metal sulfonate, an oil-soluble divalent metal phenate, and a water-soluble metal salt of an organic acid.

It was entirely unexpected that a readily emulsifiable,

rust-inhibited lubricating oil composition could be obtained in accordance with the present invention.

The oil-soluble divalent metal sulfonates used herein include alkaline earth metal sulfonates, wherein the sulfonic acids from which the salts are derived have molecular weights ranging from 400–700. It is preferred that the molecular weights of the sulfonic acids used in the formation of the sulfonates be from 450 to 550. The metal sulfonates used herein include the metal salts of synthetic sulfonic acids and petroleum sulfonic acids; and these may be exemplified by calcium white oil benzene sulfonate, calcium dipolypropene benzene sulfonate, calcium mahogany petroleum sulfonate, calcium triacontyl sulfonate, calcium didodecylbenzene sulfonate, etc.

Preferably, the metal sulfonates are somewhat basic; that is, the sulfonates contain a greater amount of metal than that necessary for the neutralization of the sulfonic acids from which they are derived. For example, a metal mahogany petroleum sulfonate may contain as much as 100 mol percent metal in excess of that essential for the formation of neutral metal mahogany petroleum sulfonate.

Phenates which are contemplated for use herein in combination with the above-noted sulfonates include oil-soluble divalent metal salts of phenol and substituted phenols, and oil-soluble sulfurized divalent metal salts of phenol and substituted phenols. Examples of these include the sulfurized alkaline earth metal phenates, such as sulfurized calcium salts of octylphenol, decylphenol, dodecylphenol, pentadecylphenol, hexadecylphenol, octadecylphenol, triacontylphenol, polypropenephenol, etc.

Divalent metal phenates which are particularly effective herein in combination with divalent metal sulfonates in the formation of water-emulsifiable lubricating oil compositions are the basic sulfurized divalent metal phenates described in Walker-Shiells U.S. Patent 2,680,096. These particular sulfurized metal phenates have metal contents as great as 100% or more in excess of the metal contents of neutral sulfurized metal phenates.

The water-soluble divalent metal salts of organic acids of the emulsifiable lubricating oil compositions of this invention include the alkaline earth metal salts, such as calcium salts, of organic acids, such as formic acid, acetic acid, propionic acid, butyric acid, hydroxybutyric acid, maleic acid, salicylic acid, phthalic acid, etc. It is preferred to use the calcium salts of the aliphatic monobasic acids containing from 1 to 4 carbon atoms.

Suitable lubricating oils which are useful in the formation of the water-in-oil emulsions of this invention include a wide variety of lubricating oils, such as oils which can be manufactured by solvent treating, acid treating, etc.; various crude oils, such as paraffinic, naphthenic, or mixed base crude oils, or such as those which can be obtained by synthesis, e.g., the Fischer-Tropsch process. Lubricating oils also include those derived from coal products and synthetic oils, e.g., alkylene polymers, dicarboxylic acid esters, and liquid esters of acids of phosphorus and silicon. The preferred lubricating oils for this invention are the petroleum oils of lubricating viscosity.

In the formation of the water-emulsifiable lubricant herein, the lubricating oil is present as a major component of the composition, that is, in an amount of about 60% to about 98%, by weight; the water-soluble alkaline earth metal salts are present in amounts of about 0.2% to about 12%; the sulfonates are present in amounts of about 0.5% to about 5%; and the phenates are present in amounts of about 0.5% to about 5%, with the minimum total amount of sulfonate and phenate being 1%, and the maximum total amount of sulfonate and phenate being about 10%.

The preferred amounts of the above components are as follows: lubricating oil, about 75% to about 90%, by weight; water-soluble organic acid salt, about 4% to about 9%, by weight; sulfonates, about 1.5% to about 2.5%, by weight; and phenates, about 1.5% to about 2.5%, by weight.

Thus, the emulsion lubricating compositions prepared from the above-described emulsifiable lubricating oil compositions may contain from 2% to 60%, by weight, water; 30% to 98%, by weight, of an oil of lubricating viscosity; 0.5% to 4%, by weight, of sulfonate; 0.5% to 4%, by weight, of phenate; and from 0.2% to 10%, by weight, of the water-soluble salts of organic acids.

It is particularly preferred that the total amounts of sulfonates and phenates present in the water-oil emulsion lubricant do not exceed a maximum amount of 6%. Water-oil emulsion lubricants containing total amounts in excess of about 6%, by weight, tend to be unstable.

The mol ratios in which the sulfonates and phenates are present in the emulsifiable lubricant herein are critical; that is, the stability of the water-in-oil emulsions prepared from the emulsifiable lubricants of this invention is dependent on the sulfonate-phenate mol ratio. Although the sulfonate-phenate mol ratios can have values varying from 0.5 to 2.0, it is preferred that the sulfonate-phenate mol ratios have values varying from 0.75 to 1.25.

The water-oil emulsion lubricants from which the emulsifiable lubricants of the present invention are obtained contain as much as 60% water, by weight. That is, the water-oil emulsion can contain as much as 60% water and, by substantial removal of the water phase, a composition containing about 0% water is obtained.

The water may be removed by distillation at atmospheric pressures, by flashing removal through changes of pressures, or by other available means.

A water-in-oil emulsion lubricant can be obtained by forming an admixture comprising an aqueous solution of an oil-soluble salt of an organic acid (the water content being such as to result in an emulsion containing a maximum of about 60%, by weight, of water); an oil of lubricating viscosity; an oil-soluble divalent metal sulfonate; and an oil-soluble divalent metal phenate at temperatures in the range of about 90° F. to about 200° F., followed by cooling to room temperature. (When water-oil emulsions are prepared with the lower concentrations of the water-soluble salts of organic acids, the temperature of preparation may be as low as room temperature.) From this water-oil emulsion can be prepared a substantially water-free composition which is re-emulsifiable. The water-oil emulsion is heated to a temperature at which the water vaporizes (for example, distillation) for a time sufficient to remove substantially all of the water phase. It is preferred to heat to a temperature less than 230° F. at atmospheric pressure (or temperatures equivalent thereto at increased or reduced pressures).

The following examples illustrate the preparation of the lubricating compositions of this invention.

EXAMPLE 1

8 grams of a 40% lubricating oil solution of a basic sulfurized calcium alkyl phenate (the concentrate containing 2.9% sulfur and 4.5% calcium, and the alkyl group being derived from a tetrapropylene polymer and containing an average of 12 to 14 carbon atoms), and 8 grams of a 40% lubricating oil solution of a slightly basic calcium petroleum sulfonate having a molecular weight of about 1040 (the concentrate containing 2.35% calcium) was blended into 276 grams of a California naphthenic base 60 VI SAE 30 oil. To this oil composition was slowly added 108 grams of 26% aqueous solution of calcium acetate monohydrate, keeping the temperature between 140° F. to 160° F. The resulting emulsion was passed through a Manton-Gaulin homogenizer at 4000 p.s.i. The effluent emulsion was rapidly cooled to 95° F. The resulting composition contained 1.76% calcium, 0.47% sulfur; had a neutralization number (mgs. KOH per gram sample) of 46.4, and a sulfated residue (by the ASTM D-874 method) of 5.92%.

EXAMPLE 2

The water-in-oil emulsion of Example 1, above, was heated on a steam plate until substantially all of the water phase had been removed by distillation, then cooled to room temperature. The resulting emulsifiable lubricant contained 2.17% calcium.

In the dehydration step of forming the emulsifiable lubricating oil compositions, it is preferred that the temperatures do not exceed (are less than) 230° F. at atmospheric pressures.

80 grams of water was then added to the above oil composition, and by simple stirring means the water-in-oil emulsion lubricant of Example 1 was again formed. Although, for reasons of conserving time, it is preferred to use mechanical mixing means to re-emulsify the water, an emulsion can be obtained by vigorous hand stirring.

EXAMPLE 3

A stable water-oil emulsion lubricant containing 60% water was prepared by vigorously stirring at temperatures between 140° F. and 160° F. a mixture consisting of 2 grams of a 40% oil concentrate of basic sulfurized calcium alkyl phenate (the alkyl group derived from a polypropylene polymer having an average of 12 to 14 carbon atoms, and the concentrate containing 4.5% calcium, by weight, and 2.9% sulfur); 2 grams of a 40% oil concentrate of a slightly basic calcium petroleum sulfonate having a molecular weight of about 1040 (the concentrate containing 2.35%, by weight, calcium); 7 grams of calcium acetate monohydrate; 60 grams of water; and 29 grams of a California naphthenic SAE 30 base oil.

Table I hereinbelow presents data showing the criticality of the sulfonate-phenate mol ratios in forming stable water-oil emulsions from the emulsifiable lubricating oil compositions of this invention.

The water-in-oil emulsions used in obtaining the data of Table I were prepared according to the process described in Example I. The emulsions were then allowed to stand in open vessels at the designated temperature for the noted period of time. The relative stability of the emulsions was shown by the amount of "skin" which formed on the surface of the emulsions. The greater the amount of "skin," the less stable was the emulsion. This "skin" was similar to that formed in an open can of paint which has been standing as such for a period of time.

Table I

Experiment No.	Sulfonate-Phenate Mol Ratio	"Skin" after 72 hours at 110° F.
1	0.8	Trace.
2	1.6	Trace.
3	0.8	Trace.
4	1.2	Medium.
5	0.5	Medium.
6	0.8	Trace.
7	0.8	Heavy.
8	3.2	Heavy.

The emulsion lubricant of Example 1 hereinabove was tested in a Lauson gasoline engine. The test was carried out as follows: A single cylinder Lauson gasoline spark-ignition engine, 2⅝ inch bore and 2½ inch stroke, loaded with a three-phase induction generator, was operated under extremely severe conditions designed to develop fully the tendency of the lubricant to deteriorate with gum formation and piston ring sticking. The engine was operated at 1200 r.p.m., the engine jacket temperature was maintained at 375° F., the emulsion lubricant was maintained at 225° F., and the engine was inspected after a 30-hour period of operation. After this operation, the piston skirt was clean, with negligible gum deposits.

For determination of the anti-rusting characteristics of the compositions, steel cans were sandblasted, and lubricating emulsions described hereinabove were placed therein for a period of two weeks at 110° F. No rust was noted after this period.

It is particularly remarkable that the phenate-sulfonate water-in-oil emulsion compositions of this invention leave no residual deposit after evaporation of the water phase. The calcium acetate appears to be peptized in the oil-sulfonate-phenate composition. When treated in exactly the same manner as described in Example 2 hereinabove, a commercially available emulsion lubricant left large granular deposits of calcium acetate, and, after numerous attempts, the composition remaining could not be re-emulsified.

I claim:

1. A stable water-in-oil emulsion lubricant consisting essentially of from about 30% to 98%, by weight, of a petroleum lubricating oil, from 2% to 60%, by weight, of water, from 4% to 8%, by weight, of a water-soluble calcium salt of an aliphatic monobasic acid containing from 1 to 4 carbon atoms, from 1.5% to 2.5% of an oil-soluble calcium petroleum sulfonate, and from 1.5% to 2.5% of an oil-soluble sulfurized calcium alkyl phenate, wherein the alkyl radical is derived from propylene polymers having an average of about 12 carbon atoms, and wherein the sulfonate-phenate mol ratio has a value from 0.75 to 1.25.

2. A stable water-in-oil emulsion lubricant consisting essentially of from about 30% to 98%, by weight, of a

petroleum lubricating oil, from 2% to 60%, by weight, of water, from 4% to 8%, by weight, of calcium acetate, from 1.5% to 2.5% of an oil-soluble calcium petroleum sulfonate, and from 1.5% to 2.5% of an oil-soluble sulfurized calcium alkyl phenate, wherein the alkyl radical is derived from propylene polymers containing about 12 carbon atoms, wherein the sulfonate-phenate mol ratio has a value from 0.75 to 1.25.

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