United States Patent Office

3,377,281

Patented Apr. 9, 1968

3,377,281

LUBRICATING COMPOSITION

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No Drawing. Filed Feb. 26, 1965, Ser. No. 435,707
4 Claims. (Cl. 252—32.7)

The present invention relates to mineral lubricating oils having improved detergent-dispersant properties and more particularly to mineral lubricating oils containing small amounts of each of a combination of two different types of basic alkaline earth metal sulfonates and an ashless polymeric detergent.

With the advent of higher compression internal combustion engines and increased horsepower it has become common practice to incorporate into lubricating oils a variety of additives to insure successful operation of the oil under severe conditions. These additives include detergent-dispersants, corrosion inhibitors, antioxidants, pour depressors, etc. each of which is generally employed to impart a particular characteristics to the oil. Unfortunately, however, while many of the proposed additive agents improve mineral lubricating oils, quite frequently these lubricating oil compositions have not been entirely satisfactory for commercial use since apparently an additive agent which imparts a beneficial effect of one type may impart a detrimental effect with respect to one or more of other desired characteristics. For example, many additive combinations fail to meet the low temperature dispersancy characteristics required by the Ordnance MIL–L–2104B specification. Other additive combinations although meeting the low temperature detergency qualification fail to come up to the required standards in the other properties required by this specification.

It has now been found that the addition to mineral lubricating oils of small amounts of each of an oil-soluble basic calcium aromatic sulfonate, an oil-soluble, overbased calcium aromatic sulfonate and certain oil-soluble alkenyl succinimides provides a composition which not only possessess highly desirable detergent-dispersant properties but also on addition thereto of an antioxidant and a pour depressor, readily passes the Ordance MIL–L–2104B specification.

The two calcium aromatic sulfonates of the invention are obtained from aromatic oil-soluble sulfonic acids, preferably having an average molecular weight of about 350 to 600 such as the sulfonic acids produced in the treatment of petroleum hydrocarbons usually boiling primarily in the range from 600 to 1000° F. with a sulfonating agent such as sulfuric acid. The petroleum sulfonic acids produced by the acid treatment are composed to a large extent of aromatic hydrocarbons having either one or two aromatic rings per molecule, possibly with one or more long-chain alkyl groups containing from about 8 to 24 or more carbon atoms attached to the ring nucleus. However, other useful aromatic sulfonic acids are the synthetic alkaryl sulfonic acids prepared by the reaction of paraffin chains of 8 to 24 carbons or more with aromatic nuclei followed by sulfonation with fuming sulfuric acid. The preferred sulfonic acids are the mahogany sulfonic acids.

The basic calcium sulfonate of the invention can be prepared by neutralizing the aromatic sulfonic acid with an excess of a calcium compound over the stoichiometric

amount required for neutralization. The basic calcium sulfonate contains about 1 to 5 percent by weight calcium, has a measureable titratable alkalinity and a base number of generally about 10 to 60, preferably 20 to 50. By base number is meant the quantity of acid expressed in terms of the equivalent number of milligrams of potassium hydroxide required to neutralize one gram of sample, titrating electrometrically according to ASTM–D–664. Generally at least about 2 equivalents of the calcium neutralizing compound are reacted; however as little as about 1.1 equivalents may be employed, if desired. Usually little is gained by using more than about 4 equivalents of the calcium compound. When desired, the high base strength of the basic calcium sulfonate can be decreased by further reacting with CO_2 without decreasing the neutralizing power for strong acids. More specifically, a suitable basic calcium sulfonate can be prepared by sulfonating a sweet West Texas gas-oil of 150 SUS at 100° F., viscosity and an average molecular weight of 450 with three 50 pounds per barrel oleum dumps. The oil solution is decanted from the insoluble sludge and the clear oil solution of sulfonic acids is neutralized by adding a slurry of about 2 equivalents of calcium oxide in twice its weight of water. The water is topped off and the product filtered clear to obtain a basic calcium sulfonate concentrate in gas-oil containing about 1 to 5% calcium and having a base number of 10 to 50.

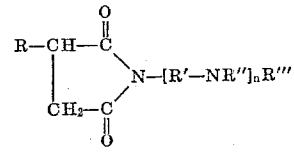
The overbased calcium aromatic sulfonates of the present invention, like the basic calcium sulfonates described above, also contain an excess of calcium above that required for neutralization to prepare the normal salt but are further distinguished in that the overbased calcium sulfonates have a base number of about 200 to 500, preferably about 250 to 400, and contain about 8 to 30 weight percent calcium. The overbased salts can be obtained by employing neutralization methods of the art known to provide a calcium aromatic sulfonate having a base number in the described range.

One method comprises employing as a starting material a basic calcium aromatic sulfonate, as described above, and subjecting the basic calcium sulfonate to treatment with carbon dioxide followed by reaction with calcium methylate. More than one of such successive carbonylation and calcium methylate reactions may be necessary to provide a calcium sulfonate having the defined base number.

According to this method the basic calcium sulfonate may be dissolved in a suitable mineral oil and reacted with an excess of carbon dioxide, usually at a temperature of about 150 to 250° C., for a time sufficient to effect reaction of one mole of carbon dioxide per mole of basic calcium sulfonate. When the carbonylation has been completed, the reaction mixture is cooled to from about 25° C. to 60° C. and a solution of calcium methylate, usually in methanol, is added in an amount sufficient to provide at least about 1 equivalent of calcium per mole of basic calcium sulfonate. The reaction mixture is then reheated at a temperature of about 150 to 250° C. After complete removal of uncombined methanol, the reaction mixture is filtered to provide the overbased calcium sulfonate in oil solution. An overbased calcium sulfonate of greater calcium content and base number can be prepared by subjecting the product thus prepared to further carbonylation and calcium methylate treatments.

Another method of preparing the overbased calcium sulfonates is described in U.S. Patent No. 3,150,088 to M. W. Hunt, Gerald L. Nield and Richard M. Tillman issued Sept. 22, 1964.

The oil-soluble alkenyl succinimides of the invention can be represented by the following formula:



wherein R is an alkenyl radical of about 30 to 200 carbon atoms; R′ is a divalent alkylene radical of 2 to 4 or more carbon atoms; R″ and R‴ hydrogen or lower alkyl radicals of say 1 to 4 carbon atoms; and *n* is an integer having a value of 1 to 6, preferably 2 to 4. When *n* is 1, R″ and R‴ are lower alkyl and when *n* is greater than one, R″ and R‴ are hydrogen. R is preferably a polymer of an α-monoolefin of 2 to 5 carbon atoms, wherein the polymer has a molecular weight from 400 to 3000, more particularly from about 900 to about 1200.

The alkenyl succinimide component of the invention can be prepared by first reacting the polyolefin with maleic anhydride to form an alkenyl succinic anhydride and then reacting the resulting anhydride with a suitable polyamide. These polyamides include dialkylaminoalkylamines and polyalkylenepolyamines.

Examples of suitable dialkylaminoalkylamines are dimethylaminomethylamine, dimethylaminoethylamine, dimethyl aminopropylamine, dimethylaminobutylamine, diethylaminopropylamine, diethylaminoamylamine, dipropylaminopropylamine, methylpropylaminoamylamine, propylbutylaminoethylamine, etc. Non-limiting examples of polyalkylene polyamines are diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, hexapropyleneheptamine, tetrabutylenepentamine, etc.

The reaction of the polyolefin with maleic anhydride and the reaction of the resulting alkenyl succinimide in turn with the polyamine are reactions well known in the art having been described in many publications as, for instance, U.S. Patent 3,018,291, and British Patent No. 922,831. These patents along with U.S. Patent Nos. 3,018,250; 3,024,195 and 3,131,150 described N-substituted alkenyl succinimides of the type considered suitable for use in the composition of this invention.

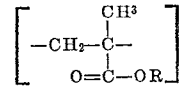
Each of the additives of the invention is added to the mineral oils in small effective amounts which may vary depending upon the particular mineral oil employed. The basic calcium sulfonate and the overbased calcium sulfonate are added in amounts that provide the final composition with a minimum total base number of at least about 2, preferably up to about 7.

The ratio of basic sulfonate to overbased sulfonate is such that about 5 to 25%, preferably 5 to 15%, of the total base number is provided by the basic sulfonate component while about 75 to 95%, preferably 85 to 95% of the total base number is provided by the overbased sulfonate. Ordinarily the amounts employed usually fall in the range of about 0.2% to 3% by weight of the basic sulfonate and about 0.1 to 1% by weight of the overbased sulfonate. The weight percent in each case is on a dry soap basis. The N-substituted alkenyl succinimide component is usually added in an amount of about 0.25% to 2.5%, preferably 0.1 to 1.5%, by weight on a dry basis.

The mineral oil base stock used in the present invention is of lubricating viscosity, e.g. 35 to 225 SUS at 210° F. and may be solvent extracted, solvent refined, acid treated, hydrogenated, a combination thereof, or an oil obtained in accordance with conventional methods of treating lubricating oils. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes, shale oils, or, if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed. A particularly suitable base oil is a blend of solvent-treated Mid-Continent neutral and bright stock having a viscosity index of about 95.

In addition to the three additives discussed above, other additive agents such as pour depressors, antioxidants, antifoam additives and the like can be employed to improve the oil in one or more respects. For example, to improve the antioxidant properties of the composition of the invention, nickel and zinc dithiophosphate diesters which are obtaned from a wide variety of diester dithiophosphoric acids conventionally prepared by reacting a sulfide of phosphorous, such as phosphorous pentasulfide, with an alcohol, phenol or mercaptan. The organic groups in the acid esters may be aryl, alkyl, aralkyl or cycloalkyl groups which contain from about 4 to 20 carbon atoms, preferably about 6 to 14 carbon atoms, and the organic groups may be further substituted if desired. A suitable zinc dithiophosphate which may be employed is the zinc salt obtained from a mixed dithiophosphate prepared by reacting a technical mixture of C_7 secondary and C_6 primary alcohols, mainly the former, with phosphorous pentasulfide. Nickel dithiophosphates which can be employed may be prepared from a di-2-ethylhexyl dithiophosphate obtained by reacting a technical mixture of 2-ethylhexanol with phosphorous pentasulfide. The zinc and nickel dithiophosphates are used in the lubricating compositions in a minor amount sufficient to inhibit oxidation and bearing corrosion and in most instances the amount employed provides about 0.02 to 0.2 percent by weight of phosphorous to the oil in which it is incorporated.

Preferred additives for improving pour point and viscosity index in lubricating oils are the methacrylate type additive agents. These additives are the oil-compatible methacrylate ester polymers which have the formula:



in which R is an alkyl group of 4 to 20 carbon atoms and *x* is the number of molecules condensed together to form a high molecular weight polymer of 5,000 to 20,000 molecular weight. These materials include a series of commercially available polymers known as the "Acryloids" some of which are described in U.S. Patent No. 2,710,842.

Anti-foam agents are particularly desirable in the lubricating composition for inhibiting foam and gas entrainment and for this purpose silicone oxide condensation polymer products such as polymers of dimethyl silicone, methyl phenyl silicone, ethyl butyl silicone, etc. can be employed. These materials and their method of preparation are well known to the art and are described in U.S. Patent No. 2,662,055. The silicone oxide anti-foam agents are conveniently handled as a 10 percent concentrate in a hydrocarbon solvent such as kerosene, and in the specific examples shown below a concentrate was prepared by dissolving 10 grams of dimethyl silicone polymer in a sufficient amount of kerosene to make up a total volume of 100 cc. The silicone polymer concentrate is preferably employed in the hydrocarbon base oil in a proportion of about .00001 to 0.05 percent by weight.

The lubricating oil compositions of the invention are further illustrated by the following example.

EXAMPLE

A lubricating oil was prepared having the following composition:

Base oil:	Vol. percent
Solvent refined Mid-Continent neutral oil, 200 SUS at 100° F.	59
Solvent refined Mid-Continent bright stock, 150 SUS at 210° F.	41

Additives:	Percent
Zinc diphenyldithiophosphate [1]	1.8
Basic calcium mahogany sulfonate [2]	1.0
Overbased calcium mahogany sulfonate [3]	1.44
Diethylenetriamine alkenyl succinimide [4]	1.0
Methacrylate polymer [5]	0.02
Dimethyl silicone polymer, KV at 100° C. of 200	0.0001

[1] Prepared from 4 moles of phenol with one mole of P_2S_5 at 160–170° F.

[2] A 45% concentrate in mineral oil solution which analyzes: 3% calcium; Base No. 28.0.

[3] As an approximately 20% concentrate in mineral oil solution analyzing approximately 11.5% by weight calcium and having a Base No. 275.

[4] An approximately 48% concentrate in mineral oil of the reaction product prepared by reacting polyisobutylene having a molecular weight of approximately 1000 with maleic anhydride and then reacting the resulting polybutenyl succinic anhydride with teraethylenepentamine.

[5] Acryloid 150; a 40% concentrate in mineral oil of methacrylate polymer in which the ester groups are derived from a mixture of alcohols in the C_5 to C_{14} range.

The total Base No. of the oil composition was 2.85, about 8% of which was provided by the basic calcium mahogany sulfonate and about 92% of which was provided by the over-based calcium mahogany sulfonate.

In accordance with the requirements of Ordnance MIL-L-2104B the oil composition was subjected to the following tests:

(A) Caterpillar 1H test—In this test the grooves are rated for deposits—a minimum of 30% top groove filling being allowable. The test is run for 480 hours.

(B) Low temperature sludge dispersancy test.—This test is run for 180 hours.

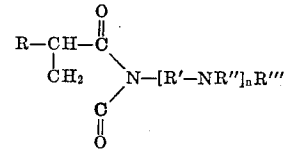
(C) Oldsmobile Sequence II rust test.

(D) CLR L–38 oxidation test.

Caterpillar 1H test	Pass—0.1% top groove filling.
Low temperature sludge test	Pass—total sludge 47.1.
Oldsmobile Sequence II rust test	Pass—9.6 average rust.
L–38 test	Pass—Cu-Pb bearing weight loss 31 mgs.

It is claimed:

1. A lubricating oil composition consisting essentially of a major amount of a mineral oil of lubricating viscosity, about 0.2% to 3% by weight of a basic calcium aromatic sulfonate having a base number of about 10 to 60 and a calcium content of about 1 to 5%, about 0.1 to 1% by weight of an overbased calcium aromatic sulfonate having a base number of about 200 to 500 and a calcium content of about 8 to 30%, and about 0.25 to 2.5% by weight of an alkenyl succinimide having the formula:



wherein R is an alkenyl radical of about 30 to 200 carbon atoms, R′ is a divalent alkylene radical of about 2 to 4 carbon atoms, R″ and R‴ are selected from the group consisting of hydrogen and a lower alkyl radical and n is an integer having a value of 1 to 6, with the proviso that when n is 1, R″ and R‴ are lower alkyl and when n is greater than 1, R″ and R‴ are hydrogen, said composition having a total base number of about 2 to 7 with said basic calcium aromatic sulfonate providing about 5 to 25% of said total base number and said overbased calcium aromatic sulfonate providing about 75 to 95% of said total base number.

2. The composition of claim 1 which contains a small amount of zinc dithiophosphate diester in which the organic groups contain from about 4 to 20 carbon atoms, said amount being sufficient to provide a phosphorous level of from about 0.02 to 0.2% by weight and about .001 to 1 percent by weight of a methacrylate ester polymer in which the ester radical contains 4 to 20 carbon atoms.

3. The composition of claim 2 wherein the basic calcium aromatic sulfonate is a basic calcium mahogany sulfonate having a base number of 20 to 50 and the overbased calcium aromatic sulfonate is an overbased calcium mahogany sulfonate having a base number of 250 to 400.

4. The composition of claim 3 wherein the basic calcium mahogany sulfonate provides about 5 to 15% of the total base number and the overbased calcium mahogany sulfonate provides about 85 to 95% of the total base number.

References Cited

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