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MINERAL OIL COMPOSITIONS

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This invention relates to new and improved mineral oil compositions.

In accordance with this invention it has been found that by admixing the oil-soluble reaction product of carbon dioxide and a barium 2,4-dialkyl phenate, wherein the alkyl substituents contain from 5 to 10 carbon atoms, in a mineral oil composition containing the oil-soluble product obtained by reacting carbon dioxide with a basic barium salt of a long chain alkyl substituted aryl sulfonic acid the detergent-dispersant properties and the oxidation characteristics of the mineral oil when in use are materially improved.

The oil-soluble products obtained by reacting carbon dioxide with basic barium salts of long chain alkyl substituted aryl sulfonic acids are described and claimed in co-pending application Serial No. 326,133, filed December 15, 1952, of H. W. Faust, now abandoned. These oil-soluble products are believed to be carbonates, however, they are of a complex nature and because of this it is not possible to state their chemical structure with absolute certainty. Thusly these products will be referred to hereinafter as carbonated basic barium hydrocarbon sulfonates.

The basic barium salts of long chain alkyl substituted aryl sulfonic acid reactants employed in preparing the carbonated basic barium hydrocarbon sulfonates are of uncertain structure. However, it is possible that they may be represented by one or both of the following formulae:

(1) $HO—Ba—SO_3—R$

(2) $(HO)_2—Ba:Ba—(SO_3—R)_2$

wherein R is a long chain alkyl substituted aromatic hydrocarbon residue. In the second of the above formulae the colon indicates that the barium contributes both electrons to form a Werner coordination compound. It is to be understood, however, that the above structural formulae are merely those which have been postulated on the basis of analytical results and it is not intended that they in any manner should limit the scope of the invention.

The long chain alkyl substituted aryl sulfonic acids employed in making the aforedescribed basic barium hydrocarbon sulfonate reactant may be represented by the formula $R—SO_3—H$ wherein R is a long chain alkyl substituted aromatic hydrocarbon residue. Among the aromatic hydrocarbon nuclei contemplated are such radicals as phenyl, tolyl, ethylphenyl, cumyl, isobutylphenyl, tert. butylphenyl, xylyl, cymyl, biphenylyl, indenyl, naphthyl, and the like. By a "long chain alkyl substituent" is meant an alkyl radical containing at least 8 carbon atoms. Although any long chain alkyl substituent is contemplated, it is preferable that the substituent be a wax residue and preferably a wax residue having a chain of 20 to 30 carbon atoms. From a practical standpoint it has been found that the aromatic hydrocarbon nucleus of the sulfonic acids ($R—SO_3—H$) employed in preparing the reactants for the preparation of the carbonated

basic barium hydrocarbon sulfonates of this invention should contain not more than four long chain alkyl substituents. In general, however, those sulfonic acids wherein the aromatic hydrocarbon nucleus contains 1–3, inclusive, long chain alkyl substituents are preferred in the preparation of the reactants of this invention and it is particularly preferred that they contain but two long chain alkyl substituents.

The carbonated basic barium hydrocarbon sulfonates of this invention are prepared by dissolving a basic barium salt of a long chain alkyl substituted aryl sulfonic acid in an inert organic solvent, reacting therewith carbon dioxide, separating the water by-product produced thereby, and isolating the desired carbonated product. In that the basic barium sulfonate reactants are highly soluble in mineral oils of the type normally used in internal combustion engines it has been found convenient in preparing compositions for use in crank case lubricants to dissolve the basic barium hydrocarbon sulfonate reactant in a suitable mineral oil to form a concentrate containing, e. g. 25–75% by weight of the sulfonate reactant, and bubble carbon dioxide through the concentrated solution at temperatures from 20–150° C. The incorporation of carbon dioxide in the mineral oil solution of the sulfonate reactant does not produce a less soluble product and as a result the carbonated products can be prepared in concentrates, e. g. 25–75% by weight, of the carbonated product dissolved in mineral oil. In the practice of the present invention, however, these carbonated products will be present in minor amounts with respect to the mineral oil but in amounts sufficient to improve the properties of the oil. Generally in the practice of this invention it is preferred that the carbonated basic barium hydrocarbon sulfonate be present in amounts in the range of 0.1–10% and preferably 0.5 to 5% by weight based on the mineral oil.

As illustrative of the carbonated basic barium hydrocarbon sulfonate and preparation thereof is the following:

EXAMPLE I

A paraffin wax having an average of about 23 carbon atoms in the molecule and an ASTM melting point of about 125–127° F. is chlorinated at about 80–85° C. with gaseous chlorine until the weight of the wax is increased to about 12%.

1000 parts by weight of the so prepared chlorowax is fed into a suitable reaction vessel containing a mixture of 201 parts by weight of benzene and about 36 parts by weight of aluminum chloride catalyst over a period of 3–4 hours at a temperature maintained at 35–50° C. Thereupon the temperature of the reaction mix is raised to 85–90° C. and is held there for 2 hours. The catalyst sludge is removed and the unreacted benzene and other contaminants are separated from the sludge-free liquid by steam distillation. The product obtained upon removing the residual water apparently is a diwax-alkylated benzene.

To 1000 parts by weight of the diwax-alkylated benzene so prepared is added with agitation over a 3 hour period approximately 459 parts by weight of 25% oleum while maintaining the temperature at 45–55° C. Upon completion of the acid addition there is added approximately 105 parts by weight of water while maintaining the temperature at 50–55° C. Thereupon 1000 parts by weight of SAE-10 grade mineral oil is added to the mix while raising the temperature to 70–75° C. The reaction mixture of acid and oil is then stirred for about 30 minutes at about 75° C. Upon stopping the agitation the oily layer is separated from the aqueous layer by draining off the latter.

2129 parts by weight of the mixture of mineral oil and the diwax-alkylated benzene sulfonic acid obtained upon

separating the aqueous layer by the aforementioned draining operation is then placed in a suitable reaction vessel, and thereto is added about 509 parts by weight of barium hydroxide octahydrate. Upon completion of the addition the mix is heated to 80–90° C. and agitated at that temperature for 30 minutes.

Thereupon the mix is heated to about 125° C. and the water distilled off. Vacuum is then applied to complete the dehydration. The dehydrated mixture is then admixed with a small amount of clay and the mixture filtered through a press at 100–110° C. 2376 parts by weight of approximately a 58% by weight solution of the basic barium salt of a diwax-alkylated benzene sulfonic acid is obtained. The blend of oil and sulfonate upon analysis is found to contain about 9.4% barium.

Upon diluting this 58% by weight mineral oil concentrate of sulfonate with 2064 parts by weight of mineral oil (SAE–10 grade motor oil) there is obtained approximately a 31% by weight solution assaying about 5% barium, about 1.2% sulfur and possessing a sp. gr. of 0.96 at 60°/60° F. and a Saybolt viscosity of 65 at 210° F.

EXAMPLE II

At reduced pressure and at a temperature of 120–135° C. carbon dioxide is bubbled at the rate of about 0.8–1.0 parts by weight of CO_2 per min. into 1000 parts by weight of the 31% mineral oil solution of the basic barium salt of the diwax-alkylated benzene sulfonic acid of Example I for about 3 hours. Upon stopping the carbon dioxide addition the temperature is maintained at 105–135° C. and vacuum is applied in order to complete the removal of the water by-product. The reaction product is admixed with a small amount of clay and the mixture filtered through a press. The resultant product is approximately a 31% by weight solution of the carbonated product possessing a sp. gr. of 0.96 at 60°/60° F. and a Saybolt viscosity of 65 at 210° F. Upon analysis the carbonated product is found to contain about 5% barium and about 1.2% sulfur. The amount of carbon dioxide absorbed to form the resultant wax-like composition is about 8.1 parts by weight or approximately 1 molecular weight of carbon dioxide per 2 atomic weights of barium of the basic barium salt of the diwax-alkylated benzene sulfonic acid. The amount of water by-product produced is about 1 mol per mol of carbon dioxide absorbed.

As exemplary of other chlorinated waxes useful for the preparation of the carbonated basic barium hydrocarbon sulfonates than that specifically described in Example I are those in which the degree of chlorination has been so regulated that the final chlorinated wax contains 5–15% chlorine. By following substantially the same steps of Examples I and II and employing such chlorinated waxes, there is obtained other homologous carbonated products which are contemplated by this invention. In general any alkyl halide containing at least 8 carbon atoms, and preferably not more than 30 carbon atoms, upon reacting with an aromatic hydrocarbon such as benzene, toluene, cumene, xylene, diphenyl, naphthalene, etc., in a molecular proportion such that one to four long chain alkyl groups are introduced into the aromatic nucleus produces an alkylated aromatic hydrocarbon which upon sulfonating, forming an oil-soluble basic barium hydrocarbon sulfonate, and carbonating in the manner described heretofore provides for oil-soluble carbonated basic barium hydrocarbon sulfonates contemplated by this invention.

The oil-soluble products obtained upon reacting carbon dioxide with a barium dialkyl phenate, wherein the alkyl substituents contain from 5 to 10 carbon atoms of this invention are of a complex nature and because of this it is not possible to state their chemical structure with absolute certainty. Thusly, these products will be referred to hereinafter as carbonated barium 2,4-dialkyl phenates.

The barium 2,4-dialkyl phenates employed in making the carbonated barium 2,4-dialkyl phenates of this invention are prepared by neutralizing a 2,4-dialkyl phenol with an oxide or hydroxide of barium. Alternatively the alkali metal phenate of the 2,4-dialkylphenol may first be made, and then the phenate may be reacted with a water-soluble salt of barium to yield the barium salt by a double decomposition reaction. They may also be prepared by reacting a barium alcoholate with a 2,4-dialkyl phenol. The dialkyl phenol employed in making the barium dialkyl phenate reactants can be prepared by dialkylating phenol in known manner as for example in the presence of sulfuric acid with olefins having from 5 to 10 carbon atoms. Thus the alkyl substituents of the phenate reactants include normal and branched chain amyl, hexyl, heptyl, octyl, nonyl and decyl radicals. The preferred alkyl substituents are branched chain, that is an alkyl group branched at the carbon which is attached to the phenol nucleus or in other words secondary or tertiary alkyl groups linked to the phenol nucleus. The particularly preferred alkyl substituents are branched chain octyl and nonyl radicals, e. g. the octyl radical tt-octyl and the nonyl radical 1,3,5-trimethyl-hexyl. Olefins such as 2-methyl-butene-1, 2-methylbutene-2, pentene-1, pentene-2, 4-methylpentene-1, 4-methylpentene-2, 2-methylpentene-1, 2-methylpentene-2, hexene-1, hexene-2, hexene-3, the various isohexenes, heptene-1, heptene-2, the various isoheptenes, octene-1, octene-2, the various isooctenes such as the trimethylpentenes and 2-ethylhexene-1, nonene-1, the various isononenes such as 4,6-dimethylheptene-2 and 2,6-dimethylheptene-3, diamylene, etc., may be conveniently employed. It is preferred from the standpoint of economy to conduct the alkylation with a commercial polypropylene fraction boiling in the range of 100–180° C. and boiling for the most part between 110° C. and 155° C., having an average of 9 carbon atoms in the polypropylene radical and containing tripropylenes as the major component. This class of olefins is known commercially as "propylene trimer."

The carbonated derivatives are prepared by dissolving a barium 2,4-dialkyl phenate in an inert organic solvent reacting therewith carbon dioxide and isolating the desired carbonated product, the amount of carbon dioxide absorbed being about one mol per mol of metallic barium. In that the barium 2,4-dialkyl phenate reactants are soluble in mineral oils of the type normally used in internal combustion engines, it has been found convenient in preparing compositions for use in crank case lubricants to dissolve the barium 2,4-dialkyl phenate reactant in a suitable mineral oil to form a concentrate (e. g. 25–75% by weight) of the phenate reactant and introduce to the mineral oil solution carbon dioxide, as for example by bubbling below the surface of the solution, at a temperature from about 20–200° C. The incorporation of carbon dioxide in the mineral oil solution of the phenate reactant does not produce a less soluble product and as a result the new carbonated products can be prepared in concentrates (e. g. 25–75% by weight). In the practice of this invention, however, these carbonated products will be present in mineral oils in minor proportions, that is up to 50% by weight, sufficient to improve the properties of the lubricating oil. However, for most lubricating purposes a mineral oil containing 0.1–10% by weight of the carbonated barium 2,4-dialkyl phenate is satisfactory and amounts of from about 0.5 to about 5% by weight are preferred.

As illustrative of the preparation of the barium 2,4-dialkyl phenates as well as the carbonated derivatives of this invention is the following:

EXAMPLE III

To a suitable reaction vessel containing 109.4 parts by weight of molten phenol is added and intimately mixed 293 parts by weight of a commercial propylene trimer dis-

tilling at normal atmospheric pressure from 107–170° C., the major proportion boiling between 116° C. and 144° C. During the addition of the olefin the system is gradually cooled to about 25–30° C. To the olefin suspension of phenol is slowly added with agitation 28.5 parts by weight of 100% sulfuric acid while maintaining the temperature below about 30° C. Upon completion of the acid addition the mix is agitated for about eight hours at 25–35° C. To the mix so obtained is slowly added 2 parts by weight of water followed by 28.5 parts by weight of sodium carbonate while maintaining the temperature at about 25–35° C. Upon completion of the sodium carbonate addition the mix is heated gradually to about 150° C. and the water distilled off. Vacuum is then applied to complete the dehydration and to remove any unreacted materials. The mix is then admixed with 13 parts by weight of clay and the mixture filtered through a press at 100–110° C. A 100% yield of a light amber dialkylated product essentially consisting of 2,4-di-(branched chain nonyl) phenol is obtained. Analysis indicates that the nonyl substituents are principally secondary alkyl radicals.

EXAMPLE IV

To a suitable reaction vessel containing 100 parts by weight of the 2,4-di-(branched chain nonyl) phenol of Example III dissolved in 149 parts by weight of mineral oil (SAE–10 grade motor oil) is added and intimately mixed 24.9 parts by weight of barium as 95% barium oxide dissolved in methanol (the alcohol solution assaying about 14% barium), the temperature during the barium addition being maintained at about 75–80° C. permitting the methanol to distill off. Upon completion of the barium addition the solution is heated for about 15 minutes at 75–80° C. and then slowly heated to 150° C. to completely remove the methanol. The mass is cooled, admixed with 2 parts by weight of clay and filtered through a press. Approximately 270 parts by weight of approximately a 46.3% by weight solution of barium 2,4-di-(branched chain nonyl) phenate is obtained.

Upon diluting this 46.3% by weight mineral oil concentrate with 27.3 parts by weight of mineral oil (SAE–10 grade motor oil) there is obtained approximately at 42.1% by weight solution assaying 8.0% by weight barium and possessing a specific gravity of 0.9857 at 60°/60° F. and a Saybolt viscosity of 61.3 at 210° F.

EXAMPLE V

At reduced pressure and at a temperature of about 140–150° C. carbon dioxide is bubbled at the rate of about 0.8–1.0 part by weight per minute into 269.9 parts by weight of the 46.3% by weight solution of the barium 2,4-di-(branched chain nonyl) phenate of Example IV. The carbon dioxide addition is continued until there is obtained a positive pressure of about 10 pounds per square inch. Upon stopping the carbon dioxide addition this positive pressure is maintained for about 30 minutes and then released. The reaction product is cooled, admixed with 2 parts by weight of clay and filtered through a press. The resultant product is admixed with 14 parts by weight of mineral oil (SAE–10 grade motor oil) to give approximately a 45.1% by weight solution of the carbonated product possessing a specific gravity of 0.9987 at 60°/60° F., a Saybolt viscosity of 54.9 at 210° F. and assaying approximately 8.0% by weight barium. The amount of carbon dioxide absorbed to form the resultant carbonated product is about 6.8 parts by weight or approximately one molecular weight of carbon dioxide per atomic weight of metallic barium.

EXAMPLE VI

To a suitable reaction vessel containing 100.5 parts by weight of di(tt-octyl) phenol, i. e., di(1,1,3,3-tetramethylbutyl) phenol, a light tan colored liquid consisting essentially of 2,4-di(tt-octyl) phenol dissolved in 138 parts by weight of mineral oil (SAE–10 grade motor oil) is added and intimately mixed 24.9 parts by weight of barium as 95% barium oxide dissolved in methanol (the alcohol solution assaying about 14% barium), the temperature during the barium addition being maintained at about 75–80° C. permitting the methanol to distill off. Upon completion of the barium addition the solution is heated for about 15 minutes at 75–80° C. and then slowly heated to 150° C. to completely remove the methanol. The reaction product is then admixed with a small amount of clay and filtered through a press. The resultant product is a 47.4% by weight solution of barium 2,4-di(tt-octyl) phenate possessing a specific gravity of 0.9902 at 60°/60° F., a Saybolt viscosity of 54.6 at 210 F., and assaying approximately 8.0% by weight barium.

EXAMPLE VII

To a suitable reaction vessel containing 100.5 parts by weight of di(tt-octyl) phenol, i. e., di(1,1,3,3-tetramethylbutyl) phenol, a light tan colored liquid consisting essentially of 2,4-di(tt-octyl) phenol dissolved in 147 parts by weight of mineral oil (SAE–10 grade motor oil) is added and intimately mixed 24.9 parts by weight of barium as 95% barium oxide dissolved in methanol (the alcohol solution assaying about 14% barium), the temperature during the barium addition being maintained at about 75–80° C. permitting the methanol to distill off. Upon completion of the barium addition the solution is heated for about 15 minutes at 75–80° C. and then slowly heated to 150° C. to completely remove the methanol. The system is cooled to about 90–100° C. and placed under vacuum, whereupon carbon dioxide is introduced to the system by subsurface addition at the rate of about 0.8–1.0 parts by weight per minute until a positive pressure of 10 pounds per square inch is obtained. Thereupon the carbon dioxide addition is stopped and the system is maintained at this positive pressure for about 30 minutes and then the system is vented. The reaction product is then admixed with a small amount of clay and filtered through a press. The resultant product is a 48.3% by weight solution of carbonated barium 2,4-di(tt-octyl) phenate possessing a specific gravity of 0.9902 at 60°/60° F., a Saybolt viscosity of 54.6 at 210° F., and assaying approximately 8.0% by weight barium. The amount of carbon dioxide absorbed is about 6.8 parts by weight or approximately one molecular weight per atomic weight of metallic barium.

As exemplary of the antioxidant properties of the new compositions the following lubricating compositions containing the same weight percentage of metallic barium, respectively, are prepared and evaluated in a CRC Designation L–4–545 (described on p. 394 of the CRC Handbook 1946) engine test for oxidation stability:

Lubricant	A	B	C	D
Product of Example II (31% solution) parts by weight	3.3	3.3	3.3	3.3
Product of Example IV (42.1% solution) do	3.5			
Product of Example V (45.1% solution) do		3.5		
Product of Example VI (47.4% solution) parts by weight			3.5	
Product of Example VII (48.3% solution) parts by weight				3.5
Commercial oxidation inhibitor do	0.7	0.7	0.7	0.7
Mineral oil (SAE–30 grade) do	92.5	92.5	92.5	92.5

Table I

Lubricant	A	B	C	D
Bearing Corrosion (mgs. weight loss in metal per bearing)	526	104	193	32
Percent viscosity increase	19.7	15.7	21.7	6.4

As exemplary of the detergent-dispersant properties of the new compositions the following lubricant compositions containing the same weight percentage of barium,

respectively, are prepared and evaluated in a CRC Designation L–1–545 (described on page 347 of the CRC Handbook 1946) engine test for detergent-dispersant properties.

Lubricant	E	F	G	H
Product of Example II (31% solution) parts by weight	3.3	3.3	3.3	3.3
Product of Example IV (42.1% solution) parts by weight	3.5	------	------	------
Product of Example V (45.1% solution) parts by weight	------	3.5	------	------
Product of Example VI (47.4% solution) parts by weight	------	------	3.5	------
Product of Example VII (48.3% solution) parts by weight	------	------	------	3.5
Commercial oxidation inhibitor parts by weight	0.7	0.7	0.7	0.7
Mineral oil (SAE–30 grade motor oil) parts by weight	92.5	92.5	92.5	92.5

Table II

Lubricant	E	F	G	H
Carbon deposit on top ring groove, percent	30	10	32	Trace

The inclusion of a commercial mixture of oxidation inhibitors in the above tests is for the purpose of lowering the corrosion level in order that a more reasonable and valid comparison of the oxidation and detergent-dispersant characteristics of the new compositions could be made.

EXAMPLE VIII

At reduced pressure and at a temperature of about 90–100° C. carbon dioxide is bubbled at the rate of about 0.8–1.0 part by weight per minute into 386 parts by weight of a 48.3% by weight solution of barium 2,4-di(1,3,5-trimethylhexyl) phenate. The carbon dioxide addition is continued until there is obtained a positive pressure of about 10 pounds per square inch. Upon stopping the carbon dioxide addition this positive pressure is maintained for about 30 minutes and then released. The reaction product is cooled, admixed with 5 parts by weight of clay and filtered through a press. The resultant product is admixed with 20 parts by weight of mineral oil (SAE–10 grade motor oil) to give approximately a 47.2% by weight clear solution of the carbonated product assaying about 7.5% by weight barium. The amount of carbon dioxide absorbed to form the resultant carbonated product is about 9.7 parts by weight or approximately one molecular weight of carbon dioxide per one atomic weight of metallic barium.

EXAMPLE IX

At reduced pressure and at a temperature of about 100° C. carbon dioxide is bubbled at the rate of about 0.8–1.0 parts by weight per minute into 302 parts by weight of a 50% by weight solution of barium 2,4-di-(tertiary amyl) phenate. The carbon dioxide addition is continued until there is obtained a positive pressure of about 10 pounds per square inch. Upon stopping the carbon dioxide addition this positive pressure is maintained for about 30 minutes and then released. The reaction product is cooled, admixed with 5 parts by weight of clay and filtered through a press. The resultant clear mineral oil solution assays about 11.0% barium. The amount of carbon dioxide absorbed to form the resultant carbonated product is about 11.0 parts by weight or approximately one molecular weight of carbon dioxide per atomic weight of metallic barium.

EXAMPLE X

At reduced pressure and at a temperature of about 125–140° C. carbon dioxide is bubbled at the rate of about 0.8–1.0 part by weight per minute into 211 parts by weight of a 33.3% by weight solution of barium 2,4-di-(2-ethyl hexyl) phenate. The carbon dioxide addition is continued until there is obtained a positive pressure of about 10 pounds per square inch. Upon stopping the carbon dioxide addition this positive pressure is maintained for about 30 minutes and then released. The reaction product is cooled, admixed with 5 parts by weight of clay and filtered through a press. The resultant product is admixed with 82 parts by weight of mineral oil (SAE–10 grade motor oil) to give approximately a 25% by weight solution of the carbonated product assaying 4.2% by weight barium. The amount of carbon dioxide absorbed to form the resultant carbonated product is about 4 parts by weight or approximately one molecular weight of carbon dioxide per one atomic weight of metallic barium.

Other carbonated barium 2,4-dialkyl phenates which may be employed in preparing the novel compositions of this invention are the oil-soluble reaction products of carbon dioxide with such phenates as barium 2,4-di-sec. amyl phenate, barium 2,4-di-isoamyl phenate, barium 2,4-di-(1,3-dimethyl butyl)-phenate, barium 2,4-di-(1-methyl heptyl) phenate, etc.

It has been further found that the novel composition of this invention, i. e. a mineral lubricating oil having dissolved therein a carbonated barium dialkyl phenate and a carbonated basic barium hydrocarbon sulfonate, when admixed with an oil-soluble phosporized- and sulfurized-dicyclic terpene provides for a highly efficient and valuable lubricant composition which is further characterized by excellent stability. The concentration of the oil-soluble phosphorized- and sulfurized-dicyclic terpene in such compositions will vary from about 0.1 to about 3% by weight but in general 0.3–1% by weight based upon the mineral oil is satisfactory. In lubricating oil compositions of this invention containing an oil-soluble phosphorized- and sulfurized-dicyclic terpene optimum results are obtained wherein the weight ratio of carbonated barium dialkyl phenate to carbonated basic barium hydrocarbon sulfonate is in the range of about 1 part of the former to about 1 to 5 parts of the latter.

The oil-soluble sulfurized- and phosphorized-dicyclic terpenes referred to above are those obtained by reacting a dicyclic terpene, such as pinene, camphene, fenchene and similar terpenes containing one double bond in the molecule and comprising two ring systems, with a phosphorus sulfide at a temperature of about 100–160° C. While any phosphorus sulfide such as P_3S_6, P_4S_6, P_4S_3, P_2S_5, P_4S_7, etc., can be employed in the preparation of these reactions products, the preferred reaction products are those obtained employing phosphorus pentasulfide (P_2S_5). While the proportions of said reactants will vary depending upon the oil-solubility and oil-improvement properties desired the preferred product is that obtained by the reaction of about one mol of a phosphorus sulfide, e. g. P_2S_5, with about four mols of a dicyclic terpene, e. g. pinene, at a reaction temperature in the range of about 100°–160° C.

As exemplary of oil-soluble sulfurized- and phosphorized-dicyclic terpenes and their preparation the following is illustrative:

EXAMPLE XI

A mixture of 245 parts by weight of pinene (substantially 1.8 mols) and 220.5 parts by weight of mineral oil (SAE–10 grade motor oil) is charged into a suitable reaction vessel and is heated to 110°–115° C. While stirring, 100 parts by weight of phosphorus pentasulfide (substantially 0.45 mol) are added slowly while maintaining the temperature at 110°–120° C. The temperature of the mixture is then increased to about 150° C. and stirred at that temperature for one hour. After partial cooling of the reaction mixture there is added a small amount of clay and the mixture filtered. The filtered product is a clear red viscous oil, having a sp. gr. of 1.02 at 15.6/15.6° C., a Saybolt viscosity of 145 at

210° F. and analyzing about 4.7% phosphorus and about 13.% sulfur.

The lubricating oil stocks employed in making the new lubricating compositions of this invention are usually mineral lubricating oils of the type normally used in internal combustion engines. However, distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, as well as the synthetic oils and white oils are also useful as base stocks.

Other agents can be added to the new lubricating compositions such as dyes, pour point depressants, soaps, corrosion inhibitors, other antioxidants such as the zinc salts of dialkyl thiophosphoric acids and the sulfurized phenols, thickeners, viscosity index improvers, defoamants, resins, graphite, and the like, where desired.

While the invention has been described in respect to several embodiments it is not so limited but that variations and modifications thereof may be made by those skilled in the art without departing from the spirit or scope of the invention.

This application is a continuation-in-part of my copending application Serial Number 347,150, filed April 6, 1953.

What is claimed is:

1. A lubricating composition comprising a mineral oil fraction of lubricating viscosity having dissolved therein (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-dialkyl phenate wherein the alkyl substituents contain from 5 to 10 carbon atoms and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a long chain alkyl substituted aryl sulfonic acid, the said long chain alkyl substituents containing at least 8 carbon atoms.

2. A lubricating composition comprising a mineral oil fraction of lubricating viscosity having dissolved therein (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain alkyl) phenate wherein the branched chain alkyl substituents respectively contain from 5 to 10 carbon atoms and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a long chain alkyl substituted benzenoid hydrocarbon sulfonic acid in which the long chain alkyl substituents do not exceed a total of 4, the said long chain alkyl substituents containing at least 8 carbon atoms.

3. A lubricating composition comprising a mineral oil fraction of lubricating viscosity having dissolved therein (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain alkyl) phenate wherein the branched chain alkyl substituents respectively contain from 5 to 10 carbon atoms and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a long chain alkyl substituted benzene sulfonic acid in which the long chain alkyl substituents do not exceed a total of 3 and which alkyl substituents respectively contain from about 8 to about 30 carbon atoms.

4. A lubricating composition comprising a mineral oil fraction of lubricating viscosity having dissolved therein (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain alkyl) phenate wherein the branched chain alkyl substituents respectively contain from 5 to 10 carbon atoms and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a wax-alkylated benzenoid hydrocarbon sulfonic acid in which the wax-alkyl substituents do not exceed a total of 3.

5. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain nonyl) phenate and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid.

6. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(secondary nonyl) phenate and (*b*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid.

7. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain octyl) phenate and (*b*) 0.1 to 10% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid.

8. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and barium 2,4-di-(1,3,5-trimethyl hexyl) phenate and (*b*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid, said wax substituents containing from about 20 to about 30 carbon atoms.

9. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and a barium 2,4-di-(branched chain nonyl) phenate wherein the nonyl radical is derived from a polypropylene fraction boiling in the range of 100–180° C., having an average of 9 carbon atoms in the polypropylene radical and containing tri-propylene as the major component and (*b*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid.

10. A lubricating composition comprising a mineral oil fraction of lubricating viscosity and (*a*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting in substantially equimolecular proportions carbon dioxide and barium 2,4-di-(tt-octyl) phenate and (*b*) 0.5 to 5% by weight based on the mineral oil of the oil-soluble product obtained by reacting substantially one molecular proportion of carbon dioxide with

substantially two chemical equivalents of a basic barium salt of a di-wax alkylated benzene sulfonic acid, said wax substituents containing from about 20 to about 30 carbon atoms.

11. The composition of claim 4 containing dissolved therein a phosphorized- and sulfurized-dicyclic terpene.

12. The composition of claim 5 containing dissolved therein 0.1–3% by weight based upon the mineral oil of a phosphorized- and sulfurized-dicyclic terpene obtained by reacting substantially one molecular proportion of a phosphorous sulfide with substantially four molecular proportions of a dicyclic terpene at about 100–160° C.

13. The composition of claim 7 containing dissolved therein 0.1–3% by weight based upon the mineral oil of a phosphorized- and sulfurized-dicyclic terpene obtained by reacting substantially one molecular proportion of a phosphorous sulfide with substantially four molecular proportions of a dicyclic terpene at about 100–160° C.

14. The composition of claim 6 containing dissolved therein 0.3–1% by weight based upon the mineral oil of a phosphorized- and sulfurized-pinene obtained by reacting substantially one molecular proportion of phosphorous pentasulfide with substantially four molecular proportions of pinene at about 100–160° C.

15. The composition of claim 9 containing dissolved therein 0.3–1% by weight based upon the mineral oil of a phosphorized- and sulfurized-pinene obtained by reacting substantially one molecular proportion of phosphorous pentasulfide with substantially four molecular proportions of pinene at about 100–160° C.

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