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# CARBOXYLIC ACID DERIVATIVES AND LUBRICANTS CONTAINING THEM

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This invention relates to new and novel compositions of matter. More particularly it relates to the oil-soluble products obtained by reacting an oil-soluble basic barium salt of a long chain alkyl substituted aryl sulfonic acid with a low molecular weight carboxylic acid. This invention also relates to lubricating oil compositions containing the oil-soluble products obtained by reacting the basic barium salts of long chain alkyl substituted aryl sulfonic acids with low molecular weight carboxylic acids.

Oil-soluble metallo hydrocarbon sulfonates have been used in lubricating oils and have been found to be highly effective for the dispersing of sludge formations and prevention of lacquer deposits. While these metallo sulfonates impart desirable detergent properties to the lubricating oil, in many instances they seriously impair the oil. For example, many of these detergents increase the oxidation rate of the oil during use, thus, increasing the amount or concentration of acidic oxidation products in the oil, which in turn presents a serious corrosion problem, particularly in internal combustion engines which employ alloy bearings.

Antioxidants or oxidation inhibiting agents have been added to lubricating oils in order to prevent or inhibit the oxidation of the oil during use. However, when such are employed in conjunction with the oil-soluble metallo alkylated aryl sulfonate detergent-dispersants their (antioxidant) efficiency is substantially reduced. As a result the art has continued to seek a combination of a sulfonate type detergent-dispersant and an oxidation inhibiting agent which co-operate to produce a lubricating composition exhibiting a highly satisfactory combined antioxidant and detergent action.

In accordance with this invention it has been found that the products obtained upon reacting oil-soluble basic barium salts of long chain alkyl substituted aryl sulfonic acids with low molecular weight carboxylic acids form a new and novel class of highly useful solid products many of which are wax-like in nature. These new products function in a highly satisfactory manner as detergents in lubricating oils and at the same time do not impair the effectiveness of antioxidants when employed in conjunction therewith. The products formed are believed to be salts, however, they are of a complex nature and because of this it is not possible to state the chemical structure with absolute certainty. The new products will be referred to hereinafter as carboxylic acid derivatives of basic barium hydrocarbon sulfonates.

The basic barium salts of long chain alkyl substituted aryl sulfonic acid reactants of this invention 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 above described basic barium hydrocarbon sulfonate reactant of this invention 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 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 new compositions are prepared by dissolving a basic barium salt of a long chain alkyl substituted aryl sulfonic acid in an inert organic solvent, reacting therewith a low molecular weight carboxylic acid, separating the water by-product produced thereby, and isolating the desired 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 sulfonate reactant in a suitable mineral oil to form a concentrate containing, e. g. 25–75% by weight of the sulfonate reactant, and admix a low molecular weight carboxylic acid with the concentrated solution at temperatures from about 20° to 150° C. The incorporation of the low molecular weight carboxylic acid in the mineral oil solution of the sulfonate reactant does not produce a less soluble product and as a result the new products can be prepared and marketed in concentrates, e. g. 25–75% by weight, of the carboxylic acid derivative dissolved in mineral oil. However, in practice the new products of this invention will be present in mineral oils in minor proportions sufficient to improve the properties of the oil. For most lubricating purposes a mineral oil containing 0.25–25% by weight of the carboxylic acid derivative is satisfactory, although amounts of about 0.5–5% by weight are preferred.

As exemplary of the preparation of the new products and the new lubricating compositions the following is illustrative:

*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. This product is characterized by exceptional detergent properties.

*Example II*

To a suitable reaction vessel containing 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 is added approximately 20 parts by weight of 85.5% formic acid over a period of about 30 minutes with constant agitation. The reaction is exothermic and rises to about 37° C. during the formic acid addition. Upon completion of the formic acid addition the temperature is increased to about 130° C. and then vacuum is applied in order to complete the removal of the water by-product and any excess formic acid. The reaction product is admixed with a small amount of clay and the mixture filtered through a press. The resultant product is approximately a 32% by weight solution of the formic acid derivative possessing a sp. gr. of 0.96 at 60°/60° F. and a Saybolt viscosity of 60 at 210° F. Upon analysis the formic acid derivative is found to contain about 5% barium and about 1.2% sulfur. The amount of formic acid entering into the reaction to form the resultant wax-like composition is about 17 parts by weight or approximately 1 mol of formic acid per mol 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 formic acid reactant.

*Example III*

To a suitable reaction vessel containing 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 is added approximately 22.2 parts by weight of acetic acid over a period of about 30 minutes with constant agitation. The reaction is exothermic and rises to about 40° C. during the acetic acid addition. Upon completion of the acetic acid addition the temperature is increased to about 130° C. and then vacuum is applied in order to complete the removal of the water by-product and any excess acetic acid. The reaction product is admixed with a small amount of clay and the mixture filtered through a press. The resultant product is approximately a 32% by weight solution of the acetic acid derivative possessing a sp. gr. of 0.96 at 60°/60° F. and a Saybolt viscosity of 60 at 210° F. Upon analysis the acetic acid derivative is found to contain about 5% barium and about 1.2% sulfur. The amount of acetic acid entering into the reaction to form the resultant wax-like composition is about 22.2 parts by weight or approximately 1 mol of acetic acid per mol 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 acetic acid reactant.

As exemplary of the antioxidant properties of the new compositions the following lubricating compositions are prepared and evaluated in the Underwood Oxidation Testing Apparatus of General Motors Corp., Research Laboratories Division, Detroit, Michigan, as revised December 9, 1940:

| Lubricant Composition | A (parts by weight) | B (parts by weight) |
|---|---|---|
| Product of Example I (31 percent solution). | {0.39 sulfonate<br>{0.86 mineral oil | |
| Product of Example II (32 percent solution). | | {0.40 carboxylic acid derivative.<br>{0.85 mineral oil. |
| Commercial oxidation inhibitor. | 0.4 | 0.4. |
| Mineral oil solution of iron naphthenate. | 0.063 | 0.063. |
| Mineral oil (SAE–30 grade motor oil). | 98.69 | 98.69. |

TABLE I

| Lubricant Composition | A | | B | |
|---|---|---|---|---|
| Bearing | CuPb | CdAg | CuPb | CdAg |
| Bearing Corrosion (mgs. weight loss in metal per bearing) | 123 | 414 | 108 | 362 |
| Viscosity increase, percent | 257 | | 174 | |

The inclusion of a commercial oxidation inhibitor 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.

It has also been found that the new compositions, as distinguished from oil-soluble metallo hydrocarbon sulfonate detergents known prior hereto, can be admixed with phosphorized and/or sulfurized hydrocarbon lubricating oil antioxidants to produce stable composites exhibiting satisfactory antioxidant and detergent-dispersant properties. Phosphorized and/or sulfurized hydrocarbons of the terpene type have been found to be desirable components in lubricating oil compositions, however, when in combination with oil-soluble basic sulfonates they tend to decompose generating hydrogen sulfide. The new carboxylic acid derivatives of basic barium hydrocarbon sulfonates when admixed therewith form composites which are substantially free of this objection.

As exemplary of other chlorinated waxes useful for the preparation of the new products 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 are obtained other homologous carboxylic acid derivatives which ap-

preciably improve the properties of mineral lubricating oils. 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 three alkyl groups are introduced into the aromatic nucleus produces an alkylated aromatic hydrocarbon which upon sulfonating, forming the basic barium hydrocarbon sulfonate, and reacting with a low molecular weight carboxylic acid in the manner described heretofore results in an improved oil-soluble dispersant-detergent which upon usage in conjunction with an oil-soluble antioxidant will not impair the latter's efficiency.

The lubricating oil stocks employed in making the new lubricating composition 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.

In addition to formic acid and acetic acid other low molecular weight carboxylic acids such as propionic acid, butyric acid and the like may be employed in accordance with the process of this invention for preparing the new compositions.

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.

What is claimed is:

1. A composition comprising a hydrocarbon lubricating oil and dissolved therein from 0.25% to 75% by weight based on the oil of the oil-soluble reaction product obtained by reacting substantially equimolecular proportions of a low molecular weight aliphatic mono-carboxylic acid with a basic barium salt of a long chain alkyl substituted aryl sulfonic acid.

2. A composition comprising a mineral lubricating oil and a 0.25 to 25% by weigh based upon the oil of the oil-soluble reaction product obtained by reacting substantially one molecular proportion of a low molecular weight alphatic mono-carboxylic acid with substantially one molecular proportion 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.

3. A composition comprising a mineral lubricating oil oil and 0.25 to 25% by weight based upon the oil of the soluble reaction product obtained by reacting substantially one molecular proportion of a low molecular weight aliphatic mono-carboxylic acid with substantially one molecular proportion 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 8 to 30 carbon atoms.

4. A composition comprising a mineral lubricating oil and 0.25 to 25% by weight based upon the oil of the oil-soluble reaction product obtained by reacting substantially one molecular proportion of a low molecular weight aliphatic mono-carboxylic acid with substantially one molecular proportion of a basic barium salt of a wax substituted benzenoid hydrocarbon sulfonic acid in which the wax substituents do not exceed a total of 3.



5. A composition comprising a mineral lubricating oil and 0.5 to 5% by weight based upon the oil of the oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a wax substituted benzene sulfonic acid in which the wax substituents do not exceed a total of 3.

6. A composition comprising a mineral lubricating oil and 0.25 to 25% by weight based upon the oil of the oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a di-wax substituted benzene sulfonic acid.

7. A composition comprising a mineral lubricating oil and 0.5 to 5% by weight based upon the oil of the oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a di-wax substituted benzene sulfonic acid, said wax substituents respectively containing 20 to 30 carbon atoms.

8. The oil-soluble reaction product obtained by reacting in substantially equimolecular proportions a low molecular weight aliphatic mono-carboxylic acid with a basic barium salt of a long chain alkyl substituted aryl sulfonic acid.

9. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of a low molecular weight aliphatic mono-carboxylic acid with substantially one molecular proportion 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.

10. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of a low molecular weight aliphatic mono-carboxylic acid with substantially one molecular proportion 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 8 to 30 carbon atoms.

11. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a wax substituted benzenoid hydrocarbon sulfonic acid in which the wax substituents do not exceed a total of 3.

12. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a wax substituted benzene sulfonic acid in which the wax substituents do not exceed a total of 3.

13. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a di-wax substituted benzene sulfonic acid.

14. The oil-soluble reaction product obtained by reacting substantially one molecular proportion of formic acid with substantially one molecular proportion of a basic barium salt of a di-wax substituted benzene sulfonic acid, said wax substituents respectively containing 20 to 30 carbon atoms.

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