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OVERBASED DIALKYLBENZENE SULFONATES

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Int. Cl. C10m *1/40, 3/34*
U.S. Cl. 252—33 8 Claims

ABSTRACT OF THE DISCLOSURE

Overbased calcium dialkylbenzene sulfonate lubricating oil compositions, wherein the alkyl groups are of significantly different carbon lengths and structure. One alkyl group is branched chain of from 3 to 10 carbon atoms, while the second alkyl group is straight chain having secondary attachment to the benzene ring and is of from 17 to 21 carbon atoms. Overbasing is achieved with carbonation of basic calcium.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of applications Ser. No. 579,814 now Patent No. 3,422,161, filed Sept. 16, 1966, and Ser. No. 647,957, filed June 22, 1967 and now abandoned.

BACKGROUND OF THE INVENTION

Field of invention

Calcium salts of organic acids, particularly sulfonic acids, find wide use as detergents in lubricating oils. An improvement over the use of the calcium organic acid sulfonate has been the incorporation of basic inorganic salts, e.g., calcium carbonate, with the dispersant to act as an "alkalinity reserve," particularly, with fuels having high sulfur content. By neutralizing the strong mineral acids which are formed, sludge formation is diminished and the useful life of the detergent extended.

There are two major considerations with calcium organic sulfonate detergents, particularly highly overbased detergents. These are processability and engine performance. In the processability, considerations are the ease of sulfonation and overbasing, purification, and isolation. In engine performance, major considerations are the degree of deposits, the useful lifetime of the detergent, and compatibility with other additives.

Description of the prior art

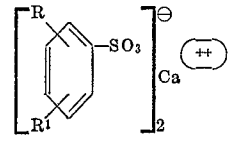
Calcium organic sulfonate salts have long been known as detergents for lubricating oils. Of somewhat shorter history, but still extensively studied, are the overbased sulfonates with increasing alkalinity values; numerous improvements in materials and processing have been reported in the patent literature.

For the most part, the organic sulfonate detergents have been derived from mineral oils and are referred to as calcium mahogany sulfonates. Other sulfonates which also have found use are the post-dodecyl benzene sulfonates and the diwax benzene sulfonates. See U.S. Patent Nos. 3,155,617, 3,235,294 and 2,379,453.

While occasionally lower alkylbenzenes—alkyl of from 1 to 4 carbon atoms—have been suggested as replacements for benzene, to be alkylated with a long chain hydrocarbon and then used in the sulfonation, these products have not been prepared. See U.S. Patent Nos. 2,721,843 and 2,762,773. The art for the most part has required two relatively long chain alkyl groups on the benzene when preparing the sulfonate for a calcium salt detergent or for overbasing.

SUMMARY OF THE INVENTION

Calcium dialkylbenzene sulfonates are provided for overbased lubricating oil detergent compositions of at least 250 mg. KOH/g. alkalinity value and can be obtained at a viscosity at 210° F. of less than about 300 SUS, wherein the calcium dialkylbenzene sulfonate has the formula:

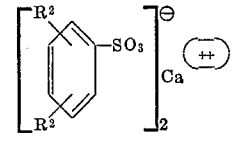


wherein R is a straight chain aliphatic hydrocarbon radical of from 17 to 21 carbon atoms having secondary attachment to the benzene ring and R^1 is a branched chain alkyl group of from 3 to 10 carbon atoms having at least one branch of from 1 to 2 carbon atoms per two carbon atoms along the longest chain. The compositions are used for compounding lubricating oils to provide detergency, particularly where high acidity is encountered in the oil.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions which are used in the compounding of the lubricating oils as detergents are comprised of the calcium organic sulfonate salt, basic calcium (calcium available for neutralizing acid) and an oil of lubricating viscosity. These materials will be considered individually.

The calcium dialkylbenzene sulfonate which is used as the dispersant has the formula:



wherein R^2 is a straight chain aliphatic hydrocarbon radical of from 17 to 21 carbon atoms, usually having at least 2 homologs present, and having secondary attachment to the benzene ring and R^3 is a branched chain alkyl group of from 3 to 10 carbon atoms, more usually of from 4 to 9 carbon atoms, having at least 1 homolog present, and more usually having at least two homologs present, and there being at least 1 branch of from 1 to 2 carbon atoms, more usually of 1 carbon atom, i.e., methyl, per 2 carbon atoms along the longest chain. The attachment of the shorter alkyl group will generally be secondary or tertiary, but may be primary, e.g., neopentyl. Particularly preferred compositions have R^3 of an average of from 5 to 8 carbon atoms.

Usually, the difference in average number of carbon atoms between the short and long chain alkyl groups will be at least 10 and more usually at least 12, and not more than 16.

The dialkylbenzene sulfonates which find use will generally have small amounts of monoalkylbenzene sulfonate, wherein the alkyl group is of from 17 to 21 carbon atoms. Rarely will the amount of the monoalkylbenzene sulfonate exceed 30% and usually the monoalkylbenzene sulfonate will not exceed 20% by weight of the total sulfonate. Generally, it will be in the range of about 5 to 20 weight percent.

The positions of the alkyl group and the sulfonate on the benzene ring in relation to each other are not critical to this invention. Generally, most of the isomeric possibilities will be encountered, with the particular isomers having the least steric hindrance being predominant. Also, there will be a broad spectrum of isomers based on the

carbon of the alkyl group bonded to the benzene ring, depending on the method of preparation and the reactants used in the preparation.

Illustrative short chain alkyl groups are isopropyl, tert.-butyl, neopentyl, diisobutyl, dipropenyl, tripropenyl, etc.

Illustrative of the long chain alkyl groups are heptadecyl, octadecyl, nonadecyl, eicosyl and uneicosyl.

Illustrative individual compositions are isopropyleicosylbenzene sulfonic acid, tert.-butylnonadecylbenzene sulfonic acid, dipropenyloctadecylbenzene sulfonic acid, diisobutyloctadecylbenzene sulfonic acid (propylene trimer)nonadecylbenzene sulfonic acid, etc.

The total number of carbon atoms in the alkyl groups will generally be in the range of at least about 20 and less than about 28. While small amounts of the dialkylbenzenes may be outside this range, the average number of carbon atoms of the alkyl groups over the total composition will be within the range.

In a preferred embodiment, a monoalkyl polypropyl benzene fraction having a boiling point range of about 318–478° F. (ASTM D 447) containing from 4 to 9 carbon atoms (an average of 6 carbon atoms) and an average molecular weight of about 167 is alkylated with a substantially straight chain C_{17-21} cracked wax α-olefin. The molecular weight of the dialkylbenzene mixture has an average value in the range of 400–410.

The average molecular weights of the dialkylbenzenes used to prepare the sulfonate will generally be in the range of about 350 to 460, more usually in the range of about 375 to 425.

The basic calcium will be predominantly present as calcium carbonate. However, from about 5 to 20% of the basic calcium present, more usually of from 10 to 15 weight percent of the basic calcium present, may be calcium hydroxide. Also, small amounts of other calcium compounds may be present which are available as basic calcium, e.g., calcium methoxide or calcium methyl carbonate.

The remaining component of the composition will be a lubricating oil, which is generally a hydrocarbonaceous oil of lubricating viscosity. Oils of lubricating viscosity are generally in the range of about 35 to 50,000 SUS (Saybolt Universal seconds) at 100° F. Normally, the oil which is used in this invention will have a viscosity of 210° F. in the range of 20 to 150 SUS. The oil may be a synthetic oil or derived from a petroleum mineral oil which is paraffin base, mixed base, naphthenic base or asphalt base. Preferably, refined oils, e.g., neutral oils, will be used.

Small amounts of other materials may also be present such as antifoaming agents. These additives will generally be present in from about 0.001 weight percent to about 0.1 weight percent.

The overbased composition will have from about 9 to 15 weight percent calcium and from about 5 to 40 weight percent of the calcium organic sulfonate. The alkalinity value will be at least about 250–400 mg. KOH/g., usually from 280 to 380 mg. KOH/g. The viscosity at 210° F. can be less than 300 SUS, usually from about 185 to 250 SUS.

DIALKYLBENZENES AND THEIR PREPARATION

The dialkylbenzenes will usually be prepared by a two-step alkylation. Although, when cumene is used which is available from natural sources, the cumene may be directly alkylated with the long straight chain alkyl group. Various functionalities may be used with the alkyl group when alkylating. The functionalities include hydroxyl, olefin, halo, oxy and the like.

The lower molecular weight branched chain alkyls are preferably derived from propylene or propylene polymers of suitable molecular weight range. Low molecular weight dimers and tetramers of two different monomers may also be used, e.g., propene and butene, propene and isobutylene, etc. The straight chain alkyls are conveniently derived from cracked petroleum wax alkene fractions or monohalogenated wax, e.g., chlorowax, of the required molecular weight.

Except for cumene, the dialkylbenzene is prepared directly from benzene with a two-step alkylation process. Benzene will be alkylated using a Friedel-Crafts catalyst, such as hydrogen fluoride or aluminum chloride. Other Friedel-Crafts catalysts include sulfuric acid, phosphoric acid and the like. The branched chain alkylating agent, e.g., alkene, will often be used first. The temperature for the alkylation will ordinarily be in the range of about 40° F. to 100° F., particularly when using hydrogen fluoride catalyst. The product will be isolated by isolating the hydrocarbon phase, washing it and distilling and collecting the desired fraction. The monoalkylbenzene is then combined with the long straight chain alkylating agent, preferably an olefin, and alkylated at a temperature of from about 75° F. to 150° F., using a Lewis acid or protonic Friedel-Crafts catalyst. Once again, the hydrocarbon phase is separated, washed and fractionated, collecting the desired fraction.

A minor amount of monoalkylbenzene may be present as already indicated. As long as the monoalkylbenzene does not diminish the molecular weight of the dialkyl benzenes below the average molecular weight specified, minor amounts of monoalkylbenzene can be tolerated.

SULFONATION

The dialkylbenzenes may then be readily sulfonated, using conventional sulfonation procedures and agents, including oleum, chlorosulfonic acid, sulfur trioxide (complexed or thin film dilution techniques) and the like.

Various methods may be used to neutralize the sulfonic acid obtained, these methods being extensively described in the art. See for example U.S. Patent Nos. 2,485,861, 2,402,325 and 2,732,344. Ordinarily, the neutralized product will be mildly overbased, having from about 1 to 50 mole percent excess of basic calcium over that required for neutralizing the acid values. Alkalinity values of these compositions will generally be in the range of about 1 to 100, more usually from about 20 to 60 mg. KOH/g.

OVERBASING OF THE CALCIUM SULFONATE

Various methods of overbasing calcium sulfonates to form superbased calcium compositions have been reported in the liteurature. See for example U.S. Patent Nos. 2,695,910, 3,282,835 and 3,155,616, as well as Canadian Patent No. 570,814. The preferred method employs a method similar to that described in U.S. Patent No. 3,155,616.

The process may be broken down into four stages: (1) first carbonation; (2) second carbonation; (3) steam stripping; and finally (4) final treatment. These stages will be considered individually and the compositions used discussed as they are involved in the process.

In the first stage, lime, methanol and a hydrocarbonaceous diluent are mixed at ambient temperatures or below.

The calcium oxide or lime is obtained by roasting calcium carbonate, calcite, marble or limestone at temperatures upwards of 2,000° F. The resulting lime is in a form in which it is readily dispersed and rapidly reacts with methanol. Calcium oxide obtained from the dehydration of calcium hydroxide may also be used, or, in some instances, hydrated lime. When referring to calcium oxide, calcium hydroxide is also intended.

The methanol used will generally have from about 0.1 to 1 weight percent water, more usually from about 0.3 to 0.7% water. The methanol will generally be present in from about 2 to 20, more usually from about 3 to 10 mole ratio to calcium oxide. Usually, the total water present in the methanol should be about 0 to 15 mole percent based on calcium oxide, more usually 5 to 10 mole percent based on calcium oxide.

The hydrocarbon diluent will be one having a boiling point higher than methanol to permit its retention when the methanol is removed during processing. The boiling point should generally be less than about 180° C. and preferably less than about 150° C. Usually, the hydrocarbon diluent will form an azeotrope with water. The usual diluents are aromatic hydrocarbons of from 7 to 10 carbon atoms, having boiling points in the range of about 100° to 180° C. These include toluene, xylene, cumene and cymene. The hydrocarbonaceous diluent is present in an amount to form about a 5 to 20 weight percent dispersion of calcium oxide in the initial composition, usually an 8 to 15 weight percent dispersion.

After mixing the above materials, carbon dioxide is introduced until from about 10 to 50%, usually 20 to 40% of the theoretical amount of carbon dioxide has been added—the theoretical amount of carbon dioxide being one mole of CO_2 per mole of calcium oxide charged. The temperature initially (when carbonation is started) is in the range of about 15° to 20° C. (if necessary), cooling the materials initially used. As the carbonation proceeds, the temperature generally rises. Usually, the temperature will rise about 10 to 12° C. if a relatively rapid rate of CO_2 introduction is maintained.

When the requisite amount of carbon dioxide has been added, the calcium dialkylbenzene sulfonate is added, generally diluted with a hydrocarbonaceous diluent. Usually, the sulfonate will be present in from about a 30 to 50 weight percent solution in a hydrocarbonaceous oil of lubricating viscosity and have from about 20 to 50 mole percent excess of basic calcium, as calcium hydroxide. Weight percent calcium will generally be from about 1.3 to about 3.5.

The amount of the sulfonate charged is based on the calcium oxide charged: from about 6 to 50 moles of calcium oxide will be used per mole of organic sulfonate, more usually from about 8 to 35 moles of calcium oxide per mole of organic sulfonate. Thus, alkalinity values can be achieved of from 250 to 400 mg. KOH/g., preferably from about 280 to 380 mg. KOH/g.

Ordinarily, the oil solution of calcium sulfonate will be further diluted with the hydrocarbonaceous diluent initially used. The amount of diluent used will depend on the amount of diluent previously added to the reaction mixture. Generally, the total amount of hydrocarbon diluents, including oils and paraffinic or aromatic low boiling solvents will be from about 8–20:1 weight ratio based on sulfonate, more usually from about 10–15:1 weight ratio based on sulfonate. The percent of the total diluent used in the first stage will generally be in the range of about 50 to 95 weight percent, more usually from about 65 to 85 weight percent. Correspondingly, the hydrocarbon diluent added with the sulfonate will range from about 5 to 50 weight percent, more usually, from 15 to 35 weight percent.

The carbonation is continued and the temperature permitted to rise, however, not to exceed the boiling point of methanol (approximately 65° C.). When the theoretical amount of carbon dioxide has been introduced or no further carbon dioxide seems to be absorbed, the reaction mixture is heated to above the boiling point of methanol and the methanol distilled off. This temperature (approximately 70° C.) is maintained until no further methanol comes over. Generally the distillation requires only a few minutes, usually not exceeding 30 minutes. Alternatively, the methanol may be removed during the steam stripping or water treatment.

The next stage in the process was referred to as steam stripping. Possibly, it is better described as treating the reaction mixture with water, near or above the boiling point of water, greater than 85° C., usually about 100° C. or higher. For steam stripping, steam is bubbled through the reaction mixture at a convenient rate. The temperature of the reaction mixture is maintained at least at 80° C. and usually at least at 90° C. to prevent the accumulation of water. Alternatively, superheated steam may be used and external heating partially or completely avoided.

The steam stripping is carried out usually for at least about 5 minutes and generally not more than about 45 minutes, more usually in the range of about 10 to 30 minutes. Some of the low boiling hydrocarbon diluent is carried over with the steam. The hydrocarbon diluent is readily separated from the water and can be dried to the extent necessary and reused.

Alternatively, water may be added and then driven off by heating the mixture to a temperature at which the water boils off, either by itself or as an azeotrope with the hydrocarbon diluent. In essence, one is forming steam in situ, rather than from an outside generator which introduces the water directly as steam. The amount of water will usually vary from about 10 to 50 volume percent of the reaction mixture, more usually from about 20 to 40 volume percent.

After the water treatment or steam stripping has been terminated, the final treatment may be carried out in various ways. The product may be filtered by adding a diatomaceous earth and then filtering or the low boiling hydrocarbon diluent stripped and the product then filtered. Also, further addition of oil may be made to obtain a product having a somewhat lower alkalinity value and viscosity. The choice of the particular route will depend on the equipment, the materials used, their physical properties, and the product desired.

The distillation will generally be carried out at temperatures below 200° C., and will usually not exceed 175° C., depending on the hydrocarbon diluents used. Preferably, when xylene is used, the temperature will not exceed 150° C.

Occasionally, the final product will be filtered again to remove any adventitious particulate matter which may still be present.

The following examples are offered by way of illustration and not by way of limitation.

Example I.—Short branched chain-long straight chain dialkylbenzene (A)

Benzene was alkylated using a tetramer polypropylene fraction and HF alkylation catalyst, a reaction temperature of about 65° F., and efficient mixing. The hydrocarbon phase was separated, washed and fractionated. The lower alkyl fraction (boiling point range 318° F. to 478° F., ASTM D 447 distillation) was collected as feed for the second stage alkylation with a mixture of straight chain 1-olefins. The average molecular weight of the above branched chain alkylbenzene was 164. This corresponds to an average of 6 carbon atoms per alkyl group in the mixture. The over-all alkyl carbon atom content corresponding to the above boiling point range is the C_4–C_9 range.

Using the above branched chain monoalkylbenzene and a substantially straight chain C_{17}–C_{21} 1-alkene fraction obtained from cracked wax, and hydrogen fluoride catalyst, the desired dialkylbenzene was produced in a stirred, continuous reactor. The 1-alkene feed had the following characteristics:

Average mol weight	268
Average number of carbon atoms per alkyl group	19
Olefin distribution, weight percent:	
C_{17}	2
C_{18}	22
C_{19}	39
C_{20}	32
C_{21}	5
Reaction conditions:	
LHSV	2
Temperature, ° F.	100
Monoalkylbenzene to α-olefin, mol ratio	2–1
Hydrocarbon to HF ratio, volume	2.3–1

After reaction the settled product was separated into an organic base and a lower HF acid phase. The crude di-

alkylbenzene organic phase was washed and then fractionated by distillation. A minor amount of forecut, mainly monoalkylbenzene, was collected up to an overhead temperature of about 450° F. at 10 mm. Hg. The balance of the distillate was the desired product, and had an average molecular weight of about 405. The difference between the average carbon atom content of the alkyl-chain types was about 13.

Example II.—Sulfonate additive preparation

The dialkylbenzene prepared as in Example I was charged to a stirred reaction vessel fitted for temperature control along with 130 neutral oil which was substantially free of sulfonatable material. The volume ratio of the two materials was 3½ to 4, respectively, and to this mixture was added over a period of several hours 2 volumes of 25% oleum. The reaction temperature was maintained at about 100° F. Two phases developed in the settled mixture, the lower being a spent mineral acid phase and the upper being the desired sulfonic acid phase.

The separated sulfonic acid-oil mixture was then neutralized with one volume of 50% aqueous caustic diluted with 15 volumes of aqueous 2-butanol. During the neutralization the temperature was maintained below about 110° F., and after completion thereof the neutral solution was heated and maintained at 140° F. during a second phase separation. Two phases developed, a lower brine-alcohol solution and an upper neutral alcohol-sodium sulfonate solution.

The neutral alcohol-sodium sulfonate phase was metathesized using concentrated calcium chloride brine to produce the desired neutral calcium dialkylbenzene sulfonate. The latter was water washed and steam stripped to remove alcohol during which operation calcium oxide was incorporated in the neutral sulfonate, thereby converting it to the desired overbased lube oil additive. The resulting basic calcium sulfonate in neutral oil contained about 42 mole percent excess of base expressed as calcium.

Example III.—Overbased sulfonate preparation

Into a reaction vessel equipped for stirring was introduced 2,000 gallons of methanol (0.5 weight percent water), 3,100 gallons of xylene and 2,700 lbs. of calcium oxide (derived from the pyrolysis of calcium carbonate); the mixture was cooled to approximately 60° F. and carbon dioxide introduced at a rapid rate until approximately 20 mol percent of the theoretical amount was added. Rapid mixing was maintained during the carbon dioxide addition and the temperature rose to about 80° F.

At the end of the initial carbon dioxide addition, 1400 gallons of a 36 weight percent calcium dialkylbenzene sulfonate in 130 neutral oil (1.52 weight percent calcium) prepared as described in Example II diluted with 1400 gallons of xylene was added to the reaction mixture and the carbonation continued until the reaction mixture refused to accept carbon dioxide. The total time for the addition of carbon dioxide was about 30 minutes and about 1800 lbs. of carbon dioxide was added. The temperature at the end of the reaction was 145° F.

The temperature was then slowly raised to 225° F. while methanol was taken overhead. When no further methanol had distilled, the reaction mixture was allowed to cool to 175° F., 100 gallons of water was added and the mixture heated and water and xylene taken overhead while the bottoms temperature was raised until it reached 250° F.

The product was then filtered hot by adding 1,250 lbs. of a diatomaceous earth and filtering the mixture. The resulting product was then stripped of xylene and the filtration repeated. The product had an alkalinity value of 285 mg. KOH/g. (11.3% total calcium) and a viscosity at 210° F. of 209 SUS.

Example IV.—Alkylation of cumene

Cumene was alkylated with 1-olefins obtained from cracked wax having an initial distillation point at 10 mm. Hg. (ASTM D 1160) at 336° F. and an end point at 619° F. and an average molecular weight of 264 (gas chromatography). The distribution of the homologs by weight percent was as follows: C_{16}—2, C_{17}—14, C_{18}—26, C_{19}—25, C_{20}—20, C_{21}—8, C_{22}—2, C_{23}—3. A continuous reactor was used and a 2.5 mole ratio of cumene to olefin employed. The pressure was maintained at 60 p.s.i.g. and the temperature at 100° F. A hydrocarbon/hydrofluoric acid volume ratio of 2.3 was employed and a reactor residence time of 15 minutes. The product was allowed to separate into two layers, the organic layer isolated and washed free of acid. The average molecular weight of the cumene-free product was 380.

The above product was sulfonated with 24% oleum as previously described in Example II and the calcium salt derived in a similar manner as described in Example II.

The equivalent weight as determined by ASTM D 1216 was 490. Total calcium weight percent was 2.96, the alkalinity value 17 mg. KOH/g.

Both the relatively neutral sulfonate and the overbased sulfonate find use as detergents and dispersants in lubricating oils. These compositions find use not only under the severe temperature conditions of the diesel engine, but also in two cycle engines and automobile internal combustion engines.

The lubricating oils with which they may be combined may be derived from natural or synthetic sources. Lubricating oils generally have viscosities of from about 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Illustrative of the synthetic oils are: hydrocarbon oils, such as polymers of various olefins and alkylated aromatic hydrocarbons; and nonhydrocarbon oils, such as polyalkylene oxides, aromatic ethers, phosphate esters and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together, whenever miscible or made so by the use of mutual solvents.

The compositions of this invention may be prepared as concentrates. When used as concentrates there will generally be present in from about 20 to 70 weight percent of Ca containing material, i.e., calcium sulfonate, carbonate and hydroxide. When the composition is compounded with a lubricating oil, the sulfonate salt, either "neutral" or overbased, will generally be present from about 0.1 to 10 weight percent, more usually 1 to 5 weight percent.

The lubricating oil compositions may also contain other additives, such as viscosity index improving agents, other detergents, oxidation inhibitors, foam inhibitors, extreme pressure agents, thickening agents, and pour point depressants.

The "neutral" sulfonate of Example II was tested under Caterpillar 1-G conditions (MIL-L-45119). The test was carried out for 480 hours. The compounded oil had a Mid-Continent SAE 30 paraffinic base oil and contained 150 mM. of total calcium per kilogram of finished oil composition. The sulfonate composition had about 38 mole percent calcium over and above that required to neutralize the sulfonic acid. Also included in the composition was 94 mM./kg. of a sulfurized calcium alkylphenate which was overbased with carbon dioxide (alkyl is polypropylene of an average of 12 carbon atoms), 10 mM./kg. of zinc O,O-di(alkylphenyl)-phosphorodithioate (alkyl being polypropylene having an average of 14 carbon atoms) and 0.001% by weight of a silicon foam inhibitor.

The results are as follows: groove deposits—1, 0.85, 0, 0, 0; land deposits—30, 0, 0, 0. (Groove deposits are rated on a basis of 0 to 100, 100 being grooves which are completely filled by deposit; land deposits are rated on a basis of 0 to 800, 800 being a completely black land.) For comparison, the same composition except that the sulfonate dispersant was derived from calcium mahogany sulfonate gave the following results: groove deposits—60.4, 3.5, 0, 0; land deposits—205, 0, 0.

In order to demonstrate the excellent detergency of the overbased sulfonate prepared in Example III, the composition was tested under Caterpillar 1–H conditions for 60 hrs. A Mid-Continent SAE 30 oil was compounded with 0.2 weight percent of a commercial polyisobutenyl succinimide of tetraethylene pentamine, 6 mM./kg. of zinc O,O-di(alkylphenyl)-phosphorodithioate (alkyl is polypropenyl of an average of 14 carbon atoms) and 60 mM./kg. of the compositions of Example III. The results are as follows: groove deposits—14, 0.3, 0, 0; land deposits—10, 0, 1; underhead—9.8. The groove deposits and land deposits are evaluated as reported previously. The underhead is evaluated on a rating of 0 to 10, 10 being completely clean. For comparison, the results using the same compositions except that the sulfonate detergent was a calcium petroleum mahogany sulfonate were as follows: groove deposits—2, 1.0, 2, 0.2; land deposits—55, 5, 5; underhead—9.

The isopropyl long chain alkylbenzene sulfonate of Example IV was tested in a Yamaha test using a 75 cc. Model YG–1 motorcycle engine. The test is carried out for 10 hours, the engine being run at 7,000 r.p.m. at a temperature of 435° F. and with wide open throttle. Using regular gasoline, a fuel-oil mixture in the ratio of 20:1 is prepared, the oil composition being a blend of detergent in SAE 40 grade base oil, such that the finished oil contained 17.05 mM./kg. of sulfonate calcium. Piston varnish, ring sticking, groove deposit numbers, land deposits and exhaust ports are all evaluated on a basis of 0 to 10 to obtain a total rating of 50 for perfect rating and 0 for a completely bad rating. A base oil will normally give a total rating of about 19.6. When using the sulfonate composition of this invention, an excellent overall rating of 37 was obtained.

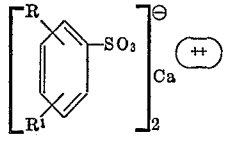
It is evident from the above results that the sulfonates, both neutral and overbased, are excellent detergents in lubricating oils, giving superior results under extremely severe conditions. Furthermore, the use of the dialkylbenzene sulfonates in the overbasing provides a bright product of good color and desirably low viscosity. Excellent compatibility with paraffinic base oils is obtained and high alkalinity values are smoothly and easily achieved by known processes. The dialkylbenzene sulfonates are readily prepared from commercially available materials and therefore provide a superior alternative to the mahogany sulfonates which are only obtained from natural sources.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

We claim:

1. An overbased calcium organic sulfonate composition, characterized by having an alkalinity value of at least 250 mg. KOH/g. comprising:

a calcium dialkylbenzene sulfonate of an average molecular weight of from 370 to 460 and of the formula:



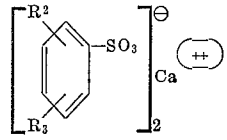
wherein R is a straight chain aliphatic hydrocarbon radical of from 17 to 21 carbon atoms having secondary attachment to the benzene ring and R^1 is a branched chain alkyl group of from 3 to 10 carbon atoms having at least one branch of from 1 to 2 carbon atoms per 2 carbon atoms along the longest chain,

a basic calcium source comprising predominantly calcium carbonate and calcium hydroxide,

and a lubricating oil,

wherein calcium is present in from 9 to 15 weight percent of the total composition and said calcium dialkylbenzene sulfonate is present in from about 5 to 40 weight percent of the total composition.

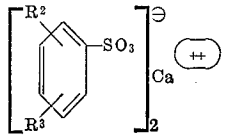
2. A composition according to claim 1, wherein said calcium dialkylbenzene sulfonate is of the formula:



wherein R^2 is a mixture having at least 2 homologs of straight chain aliphatic hydrocarbon radicals of from 17 to 21 carbon atoms, having secondary attachment to the benzene ring, and R^3 is a mixture of at least 2 homologs of branched chain alkyl groups of from 4 to 9 carbon atoms, there being at least one branch of one carbon atom per 2 carbon atoms along the longest chain.

3. A composition according to claim 2, wherein R^3 is an alkyl group of from 4 to 9 carbon atoms derived from polypropylene and wherein, when combined with benzene, the alkylbenzene has an average molecular weight of about 167.

4. A lubricating oil composition having from 0.1 to 70 weight percent of calcium dialkylbenzene sulfonate, wherein said dialkylbenzene has an average molecular weight in the range of 375 to 425, said calcium dialkylbenzene sulfonate having the formula:



wherein R^2 is a mixture having at least 2 homologs of straight chain aliphatic hydrocarbon radicals of from 17 to 21 carbon atoms, having secondary attachment to the benzene ring, and R^3 is a mixture of at least 2 homologs of branched chain alkyl groups of from 4 to 9 carbon atoms, there being at least 1 branch of 1 carbon atoms per 2 carbon atoms along the longest chain.

5. A lubricating oil composition according to claim 4, wherein R^3 is an alkyl group of from 4 to 9 carbon atoms derived from polypropylene and wherein when combined with benzene, the alkylbenzene has an average molecular weight of about 167.

6. A lubricating oil composition according to claim 4 having from 1 to 50 mole percent excess of basic calcium.

7. A lubricating oil composition having a composition according to claim 4 and an alkalinity value of from 1 to 100 mg. KOH/g.

8. A lubricating oil composition according to claim 7 having an alkalinity value of from 20 to 60 mg. KOH/g.

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U.S. Cl. X.R.

252—18

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,470,097 September 30, 196

Joe B. Lavigne et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 57, after "sulfonate" insert -- , wherein said dialkyl benzene is --; line 58, "and" should read -- , --

Signed and sealed this 1st day of December 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, J.
Commissioner of Patent