

[54] OIL SOLUBLE DIALKARYL SULFONATE COMPOSITIONS**[75] Inventors:** Mack W. Hunt; Roy C. Sias, both of Ponca City, Okla.**[73] Assignee:** Continental Oil Company, Ponca City, Okla.**[22] Filed:** Aug. 7, 1970**[21] Appl. No.:** 62,211**Related U.S. Application Data****[63]** Continuation-in-part of Ser. No. 529,284, Feb. 22, 1966, abandoned, which is a continuation-in-part of Ser. No. 446,661, April 8, 1965, abandoned.**[52] U.S. Cl.**..... 252/33, 252/389**[51] Int. Cl.**..... C10m 1/40, C10m 3/34**[58] Field of Search**..... 252/33, 389**[56] References Cited****UNITED STATES PATENTS**

2,861,951	11/1958	Carlyle.....	252/33
3,422,161	1/1969	Lavigne et al.	252/33
3,470,097	9/1969	Lavigne et al.	252/33
2,865,956	12/1958	Ellis et al.	252/33
3,537,996	11/1970	Hoist et al.	252/33

Primary Examiner—Daniel E. Wyman*Assistant Examiner*—I. Vaughn*Attorney*—Joseph C. Kotarski, Henry H. Huth, Robert B. Coleman, Jr., Bayless E. Rutherford, Jr. and Carroll Palmer**[57] ABSTRACT**

This invention relates to novel overbased and neutral

oil soluble metal dialkaryl hydrocarbon sulfonate compositions possessing low viscosity and outstanding rust inhibiting as well as water demulsification properties. Also, this invention relates to oil soluble metal dialkaryl sulfonate compounds in which the alkyl substituents contain from eight to 18 carbon atoms and are bonded to the aryl nucleus through a secondary carbon atom. In one aspect, the present invention concerns metal dialkaryl sulfonate compositions containing at least 20 weight percent metal dialkaryl sulfonate compounds in which the alkyl substituents are straight chain and contain from about eight to about 18 carbon atoms, the aryl moiety being selected from the group consisting of benzene, toluene, xylene, naphthalene and mixtures thereof. In another aspect, the present invention concerns oil soluble metal sulfonate compositions containing metal dialkaryl sulfonate compounds in which one of the alkyl substituents is a straight chain group and the other is a branched chain group, the aryl moiety being selected from the group consisting of benzene, toluene, xylene, naphthalene, and mixtures thereof. In still another aspect, this invention concerns oil soluble metal hydrocarbon sulfonate compositions containing a major amount of metal dialkaryl sulfonate compounds in which the alkyl substituents are straight chain and contain from about eight to about 18 carbon atoms, the aryl moiety being selected from the group consisting of benzene, toluene and xylene, and a minor amount of tetrahydronaphthalene sulfonate compounds, said compositions being derived from hydrocarbon compositions prepared by the disproportionation of mono-n-alkaryl compounds using aluminum chloride and/or aluminum bromide as the catalyst.

23 Claims, No Drawings

OIL SOLUBLE DIALKARYL SULFONATE COMPOSITIONS

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application, Ser. No. 529,284 filed Feb. 22, 1966, which in turn was a continuation-in-part of application, Ser. No. 446,661 filed Apr. 8, 1965, and both now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Oil soluble metal hydrocarbon sulfonate compositions both neutral and overbased are widely used as additives to lubricating oils and the like. The overbased compositions possess reserve alkalinity by reason of the inclusion in the compositions of an excess of basic metal compounds. As lubricating oil additives these compositions function as dispersing or peptizing agents, and to neutralize undesirable acidic materials which are present, or which are formed during use of the lubricating oils. The present invention broadly comprises new oil soluble metal hydrocarbon sulfonate compositions of this type, which materials are characterized as having unusually low viscosities and surprising rust inhibiting and water demulsifying properties.

2. Description of the Prior Art

According to the references cited in the parent application, Ser. No. 529,284, the following patents are the most pertinent references:

U.S. Pat. No. 3,032,501 — Ferm

This reference teaches oxyalkylated carbonated basic metal sulfonates. These basic sulfonates are derived from metal sulfonates having the formula



wherein R is a high molecular weight cyclic* (*While the specification, column 2, line 12, uses the word "cyclic" presumably acyclic is meant in view of the remainder of the specification.), straight chain or branched chain, saturated or unsaturated, essentially hydrocarbon radical having a molecular weight ranging from 150 to 800; A is an aromatic radical (e.g., benzene), $a = 1$ to 4, M is a polyvalent metal, and $x =$ valance of M. Ferm teaches that straight chain and branched chain alkyl substituents are equivalent.

U.S. Pat. 3,173,965 — Pappas et al.

This reference concerns aromatic lubricants and their method of preparation. Broadly, Pappas et al teach dialkylbenzenes, wherein the alkyl group contains from four to 21 carbon atoms, as lubricants. The alkyl groups of Pappas et al.'s dialkylbenzenes can be either straight or branched chain. While Pappas et al broadly teach "mixed alkylates," there is not the slightest suggestion in this reference that useful oil soluble sulfonates can be prepared therefrom.

U.S. Pat. No. 3,316,294 — Feighner et al.

This reference concerns a process for the preparation of water-soluble detergents. Briefly, the process of Feighner et al comprises the steps of:

a. partial halogenation of a mixture of substantially straight chain paraffin hydrocarbons,

b. alkylation of an aromatic hydrocarbon with the halogenating product of step (a).

The Feighner et al. patent does not teach alkaryl hydrocarbons having both branched chain and straight

chain alkyl groups nor does it suggest the oil soluble sulfonate compositions of the present invention.

U.S. Pat. No. 3,007,868 — Eck et al.

This reference is concerned with the preparation of light color, oil soluble alkaline earth metal sulfonates. According to the process of Eck et al. the selection of the hydrocarbon to be sulfonated is important. In column 4, line 17 to column 5, line 25, Eck et al. describe several suitable materials. In general, this disclosure is restricted to lubricating oil distillates and alkaryl hydrocarbons such as polydodecylbenzene (Col. 5, lines 10-15). In column 5, lines 10-15, the patentees teach the use of polydodecylbenzene. It is well known to those skilled in the art that polydodecylbenzene refers to alkyl-substituted benzenes wherein the alkyl groups are highly branched. The reference does not suggest alkaryl hydrocarbons of the type used in applicants' invention.

In addition to the above references cited in the parent application, the applicants are aware of U.S. Pat. No. 3,422,161 to Lavigne, et al., which concerns a sulfonatable dialkylbenzene mixture similar to the "mixed alkylate" described herein. However, this patent teaches a mixture of dialkylbenzene in which one of the alkyl substituents is a straight chain radical and the other a branched chain radical, the average carbon atom content of the aforementioned two types differing by at least four.

SUMMARY OF THE INVENTION

Broadly stated, the present invention concerns oil soluble metal dialkaryl hydrocarbon sulfonate compositions. More particularly, and in one aspect, this invention concerns oil soluble metal sulfonate compositions having viscosities of less than 750 centistokes at 210°F and comprising from about 20 to about 80 percent by weight metal di-n-alkaryl sulfonate compounds in which the alkyl substituents contain from eight to 18 carbon atoms and are, to the extent of at least 95 percent, bonded to the aryl nucleus through a secondary carbon atom, the aryl moiety of said di-n-alkaryl being selected from the group consisting of phenyl, tolyl, xylyl, naphthyl and mixtures thereof, and correspondingly from about 80 to about 20 percent by weight of nonvolatile, oil soluble hydrocarbon compounds.

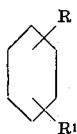
In another aspect, this invention concerns oil soluble metal sulfonate compositions containing at least 20 percent by weight metal dialkaryl sulfonate compounds in which one of the alkyl substituents is a branched chain group and the other a straight chain group, the aryl moiety being selected from the group consisting of phenyl, tolyl, xylyl, naphthyl and mixtures thereof. The sulfonate compositions are prepared from intermediate alkylate compositions prepared by either of two procedures hereinafter described.

In yet a further aspect, this invention concerns oil soluble metal sulfonates prepared from a hydrocarbon composition containing a major amount of di-n-alkaryl compounds in which the alkyl substituents contain from about eight to about 18 carbon atoms and the aryl moiety being selected from the group consisting of phenyl, tolyl, xylyl and mixtures thereof, and a minor amount of alkyl substituted tetrahydronaphthalenes of similar molecular weight, said hydrocarbon composition being prepared by the disproportionation of mono-n-alkaryl compounds using aluminum chloride and/or aluminum bromide as the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

In U.S. Pat. No. 3,316,294 assigned to the assignee of the present application, a process is disclosed which entails initially segregating a fraction of normal (straight chain) paraffin hydrocarbons from a suitable petroleum source, then halogenating such paraffin hydrocarbons and using the halo-paraffins thus produced to alkylate a suitable aromatic material, such as benzene. The alkylate reaction product is a mixture consisting predominantly of alkaryl compounds, including monoalkaryl compounds and dialkaryl compounds. The monoalkaryl product is removed from the total alkylate by vacuum fractionating, and is sulfonated to produce highly effective, completely biodegradable detergent sulfonates. The portion of the total alkylate which remains after such fractionation is a higher boiling bottoms material. The cut point between the bottoms alkylate and the detergent alkylate is about 160°C at 5 mm. Hg. The bottoms alkylate remaining after the removal of the detergent alkylate contains varying percentages of dialkaryl compounds, including the para and meta di-substituted forms in a ratio of from about 60 to about 80 mole percent of the para form to about 20 to about 40 mole percent of the meta form. As contrasted with unsuccessful attempts to sulfonate the para-dialkaryl compounds found in the bottoms alkylate produced in conventional alkylation reactions, such as that using propylene tetramer as the alkylating agent, the paradialkaryl compound content of the bottoms produced in the detergent alkylate process described in U.S. Pat. No. 3,316,294 undergoes sulfonation readily to yield oil soluble sulfonic acids which can be easily neutralized or overbased to produce valuable oil soluble sulfonates. The meta di-substituted dialkaryl compounds, of course, as previously recognized, also undergo sulfonation so that the total dialkaryl content of the bottoms alkylate can therefore be effectively sulfonated.

As an example of the structural configuration of the compounds here under discussion, where a preferred aromatic compound, benzene, is used in the detergent alkylate process, the para and meta di-substituted compounds in the bottoms alkylate can be represented by the structural formula



where R and R' are each straight chain alkyl groups containing from eight to 18 carbon atoms. The alkyl groups in the alkaryl compounds are bonded to the aryl nucleus through a secondary carbon atom, rather than the primary carbon atom. One reason for the sulfonatability of the para isomers in this bottoms alkylate appears to be that the straight chain character of the alkyl substituents favors sulfonation, while the presence of branched chain substituents has the opposite effect in para isomers. The attachment of the alkyl groups to the aryl nucleus through a secondary carbon atom also has an influence on sulfonatability, although the full extent of this influence is not now known. The presence of branched chain substituents of the type tending to resist sulfonation is characteristic of alkylates made uti-

lizing propylene tetramer, and by other methods previously in use.

The role of the straight chain alkyl groups in the bottoms alkylate used in this invention has been confirmed by experimentation in which the halogenation product used in the alkylation reaction of the invention has been used to attach a second alkyl substituent to a dodecylbenzene alkylate, having a single branched chain alkyl substituent, and the product of this reaction then subjected to sulfonation. Good sulfonation yields were obtained. In related experimentation, mono-n-alkylbenzene alkylate (detergent alkylate) made by the procedure described in U.S. Pat. No. 3,316,294 was further alkylated with propylene tetramer (branched chain dodecene) to product a dialkylbenzene alkylate in which one of the alkyl substituents was branched and the other was a straight chain group. This material also underwent sulfonation readily to yield oil soluble products. These experiments not only confirmed the importance of substitution by straight chain alkyl groups relative to the matter of susceptibility to sulfonation, but led to the discovery of novel oil soluble metal sulfonates prepared from alkylate compositions containing dialkaryl compounds in which one of the alkyl substituents is a branched chain group and the other a straight chain group.

For convenience, dialkaryl compounds having both a branched chain alkyl group and a straight chain alkyl group on the aryl moiety are referred to herein as "mixed alkylate" and the sulfonates prepared therefrom are referred to as "mixed alkylate" sulfonates.

Investigations of the bottoms alkylate material produced in the cited detergent alkylate process, have also revealed that the bottoms alkylate, in addition to di-n-alkaryl compounds, contain a significant amount of diphenyl-alkane compounds. We have noted that the extent to which these compounds are present in the bottoms alkylate is directly related to the mole ratio of alkylation reactants employed. As the mole ratio of aromatic compound to haloparaffin alkylating agent is decreased, the bottoms alkylate increases in total yield relative to the lighter detergent alkylate, and the relative amounts of the diphenylalkane and dialkaryl compounds in the bottoms alkylate shifts to favor the dialkaryl compounds. Although both materials are readily sulfonatable, the diphenylalkane sulfonate compounds are, in general, largely lost to the sludge phase overring during sulfonation, thus decreasing the yield of the overall sulfonated product. Moreover, the inclusion of diphenylalkane sulfonates in the product appears to be detrimental to the attainment of the lowest possible viscosities in the sulfonate products and may be detrimental with respect to other desired properties. It has been determined, however, that a small amount of the diphenylalkane content of the alkylate bottoms can be included in the fraction of the total bottoms subjected to sulfonation so as to increase the total yield of oil soluble sulfonate compositions produced from the bottoms. The amount of diphenylalkanes permitted to remain in this fraction should not exceed about 40 weight percent, preferably does not exceed about 25 weight percent, and most preferably is from about 5 to about 16 weight percent. In certain instances, hereinafter described in greater detail, it may be desirable to remove non-alkylated diphenylalkane compounds to the maximum extent practicable in order to impart certain de-

sirable properties to the oil soluble sulfonate products derived from the bottoms alkylate.

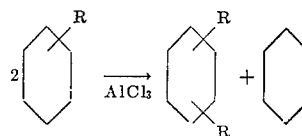
The alkylate compositions containing relatively high percentages of the specific types of di-n-alkaryl compounds found in the bottoms alkylate produced by the described detergent alkylate process may be broadly defined as hydrocarbon mixtures including at least 35 weight percent, and preferably at least 50 weight percent di-n-alkaryl compounds in which the alkyl substituents contain between 8 and 18 carbon atoms and are, to the extent of at least 95 percent bonded to the aryl nucleus through a secondary carbon atom.

As indicated, these compositions have been found to be readily sulfonatable. Moreover, it has been found that the oil soluble neutral and overbased metal sulfonates derived from the above described alkylate compositions exhibit unusual properties which are highly desirable in compositions of this type. These properties are, specifically, resistance to the formation of aqueous emulsions, good rust inhibiting properties and unusually low viscosity. The extent to which these properties are manifested is dependent upon the concentration of the di-n-alkaryl compounds in the alkylate from which the sulfonates are made.

For the purpose of preparing oil soluble metal sulfonate compositions containing a high concentration of metal di-n-alkaryl sulfonate compounds, the intermediate alkylate compositions may be prepared by a disproportionation process. Specifically, a mono-n-alkylated material, such as the detergent alkylate produced by the process described in U.S. Pat. No. 3,316,294 is subjected to a disproportionation or molecular rearrangement reaction. In the disproportionation reaction, which will be discussed in detail herein, the single alkyl substituents of the mono-n-alkaryl compounds are rearranged to yield a hydrocarbon composition consisting essentially of di-n-alkaryl compounds and alkyl-substituted tetrahydronaphthalenes. The advantage offered by the disproportionation route of obtaining the intermediate di-n-alkaryl compound-containing composition over the use of the bottoms alkylate from the detergent alkylate process as hereinbefore described is that the former process yields a composition which contains a much higher percentage of sulfonatable di-n-alkaryl compounds which can be converted in their entirety to the improved oil soluble sulfonate products of the present invention.

To more specifically characterize the disproportionation procedure, the starting material consists essentially of mono-n-alkaryl compounds in which the normal or straight chain substituents attached to the phenyl groups contain from eight to 18 carbon atoms and are bonded to the aryl nucleus through a secondary carbon atom. This material is initially heated to from about 20°C to about 120°C. A catalyst consisting of aluminum chloride, aluminum bromide, or mixtures thereof, in the amount of from 0.1 to 10 weight percent based on the weight of the alkaryl composition is then added to the hydrocarbon material, along with a very small amount of water or HCl to act as a catalyst promoter. The mixture is agitated for at least five minutes and the reaction proceeds to produce a hydrocarbon composition consisting essentially of a major amount of di-n-alkaryl compounds, and a minor amount of alkyl-substituted tetrahydronaphthalenes of similar molecular weight. The primary reaction of interest, using, for

example, mono-n-alkylbenzene as the starting material, can be represented as



where R is a straight chain alkyl group containing from eight to 18 carbon atoms and is bonded to the phenyl group through a secondary carbon atom.

The di-n-alkaryl compounds produced by the disproportionation reaction are separated from the other products of the process, and from unreacted mono-n-alkaryl compounds, by fractionation or other suitable procedure. The high purity di-n-alkaryl compounds can then be subjected to sulfonation and neutralization in accordance with conventional procedures to yield novel, oil soluble metal sulfonate compositions possessing exceptionally good rust inhibiting and water demulsibility properties, and of unusually low viscosity.

In view of the multiple aspects of the present invention, it is believed that a clearer understanding of the invention will be conveyed if the several aspects are independently considered. Initially, therefore, consideration will be given to the oil soluble metal sulfonates derived from the bottoms alkylate prepared as described in U.S. Pat. No. 3,316,294. The sulfonation, neutralization and overbasing steps which are carried out in the preparation of the compositions hereinafter described are conventional procedures well understood in the art and described in various patents and publications. Therefore, once having outlined these steps and the method of performing them in referring to one of the aspects of this invention, a detailed description thereof will not be repeated when subsequently referring to other aspects of the invention.

SULFONATES FROM BOTTOMS ALKYLATE PRODUCED IN DETERGENT ALKYLATE PROCESS

The alkylation process which simultaneously yields a detergent alkylate which can be converted to a biodegradable detergent, and a heavy or bottoms alkylate material which we have now determined can be at least partially converted to a novel oil soluble sulfonate composition is described in U.S. Pat. No. 3,316,294. As disclosed in U.S. Pat. No. 3,316,294, which is incorporated with and made a part of this disclosure, the starting materials employed comprise a mixture consisting essentially of n-paraffin hydrocarbons, a suitable halogenating material such as chloride gas, and the particular aromatic compound or compounds which are to be alkylated.

The n-paraffin fraction should consist essentially of normal paraffin hydrocarbons having a chain length of from 8 to 18 carbon atoms, and can be obtained from any petroleum derived mixture high in normal paraffins, such as a naphtha fraction corresponding to a kerosene cut. The kerosene, or other distillate relatively rich in n-paraffins and containing relatively little olefinic material, can be suitably fractionated to produce a desired fraction or normal paraffinic materials. Preferably, the paraffin fraction produced consists essentially of n-paraffins ranging in carbon atom content from about 10 to about 16 and contains no more than

10 weight percent and preferably less than 5 weight percent of the branched chain material.

Completion of the preparation of the alkylating agent used in the invention is effected by subjecting the fraction of n-paraffin hydrocarbons to contact with a suitable halogenating reagent to produce a mixture of monohalogenated n-paraffin and unsubstituted n-paraffin hydrocarbons. Preferably, the halogen substituents of the alkylating agent are chlorine, bromine, or mixtures thereof.

For convenience in further describing a preferred alkylating agent, brief reference will be made to those agents derived by chlorination of a mixture of normal or straight chain paraffin hydrocarbons. The mixture of straight chain paraffins is chlorinated in a manner to produce largely monochlorinated hydrocarbons. A suitable degree of chlorination is in the range of from about 10 to about 40 mole percent in order to attain satisfactory selectivity of the monochlorinated additives. This can be attained by reacting chlorine with the paraffin fraction in a mole ratio of between about 1:3 and 1:10. A more suitable degree of chlorination is in the range of from about 15 to about 35 mole percent. A preferred degree of chlorination is in the order of about 20 mole percent, which provides a product having a selectivity of above about 90 percent monochlorinated product.

ALKYLATION

While benzene represents the preferred aromatic compound which is to be subjected to alkylation, other aromatic compounds, such as toluene, xylene and naphthalene or mixtures of these compounds can also be employed.

The alkylation step is carried out in the presence of a Friedel-Crafts catalyst. The term Friedel-Crafts catalyst is believed to be well understood in the art and refers in general to materials such as the aluminum halides, boron trifluoride, boron trichloride, antimony chlorides, stannic chloride, zinc chloride and mercuric chloride. Of the Friedel-Crafts catalysts aluminum chloride is preferred. The preferred material, aluminum chloride, also includes "in situ" prepared aluminum chloride, in other words, the reaction product of aluminum metal and hydrogen chloride.

In some cases it is desirable to use a proton-donor promoter with the Friedel-Crafts catalyst. Suitable promoters include any material which, when added to the catalyst, yields a proton. Preferred promoters are hydrogen chloride and water.

Better control of the relative yields of reaction products is obtained if the aromatic compound to be alkylated and the alkylating stock are added to the reaction zone simultaneously, rather than at different times. Particularly, it is preferred that both alkylation reactants be added to the reaction zone prior to the addition of the catalyst thereto.

The alkylation temperature which is employed can range from about room temperature (20°-25°C) to about 80°C. The preferred temperature range is from about 40° to about 50°C. The amount of alkylating catalyst which is suitable for effecting alkylation can conveniently be based on the weight of the chloroparaffin content of the alkylating stock. On this basis, from about 1 to about 10 weight percent of aluminum chloride can be used.

The alkylation reaction can be carried out either continuously or batchwise. In either procedure, effective contact time between the catalyzed reactants is in the order of about 15 to 60 minutes and is dependent on a host of factors, including the amount of catalyst used, the ratio alkylation reactants employed, temperature, etc.

The alkylation reaction product is introduced into a suitable separator where the catalyst sludge is removed. The catalyst free alkylate is then treated by conventional procedures to remove residual acidic components and impurities. After purification treatment, the alkylate is subjected to fractionation to yield a lower boiling fraction suitable for making biodegradable detergent and a higher boiling bottoms fraction which we have found can be subjected to sulfonation and neutralization to provide the oil soluble sulfonate compositions of the present invention. Preferably, the bottoms alkylate is further fractionated prior to sulfonation in a manner hereinafter described in order to produce an alkylate containing relatively high concentration of di-n-alkaryl compounds. This alkylate can then be sulfonated, and the resulting sulfonic acids subjected to neutralization and overbasing to produce hyperbasic oil soluble sulfonates having the desirable properties hereinbefore described.

Based upon our determination that the portion of the bottoms alkylate which can be easily sulfonated to yield oil soluble sulfonic acids is made up predominantly of meta-dialkylbenzenes, and surprisingly, para-dialkylbenzenes, and our further determination that a bottoms alkylate containing as much as 40 weight percent diphenylalkane compounds can be usefully subjected to sulfonation, one of the features of the preferred manner of treating the bottoms alkylate is the control by fractionation of the amount of diphenylalkane compounds which is permitted to remain in the bottoms alkylate fraction which is to be subjected to sulfonation. The highest yield of useful oil soluble sulfonate product which can be obtained is derived from the sulfonation of a bottoms alkylate fraction which contains about 40 weight percent diphenylalkane compounds. On the other hand, we have found that it is preferred to remove the diphenylalkanes to a level of about 25 weight percent, and that where it is desired to obtain the most efficient yield of sulfonates having the most desirable properties, it is the most preferable procedure to use a relatively pure dialkylbenzene fraction from the total bottoms, such fraction being produced by reducing the non-alkylated diphenylalkane content thereof to the lowest extent practicable.

In whichever procedure is followed, the detergent alkylate is initially separated from the alkylate bottoms by fractionating the total alkylate product to remove the detergent alkylate material boiling below about 160°C at 5mm. Hg. from the higher boiling bottoms alkylate. The latter material is then topped to remove the desired amount of diphenylalkanes therefrom, which, in any event, should not permit the diphenylalkane content of the remaining bottoms to exceed 40 weight percent, and preferably 25 weight percent. The exact cut point at which the latter limit is reached will depend to some extent on the molecular weight range of the haloparaffin alkylating agent used in the alkylation reaction, but can easily be determined empirically for a particular alkylate product. In general, where the chain lengths of chlorinated n-paraffinic compounds in the

alkylating agent are between about C₁₀ and about C₁₆, topping of the alkylate bottoms to permit about 25 percent of the diphenylalkanes to remain therein is carried out to a cut point of about 235°C at 5 mm. Hg.

The described secondary fractionation or topping of alkylate is not necessary in those cases where the mole ratio of alkylation reactants employed does not exceed 2:1 aromatic to haloparaffins provided it is not the major object to obtain oil soluble sulfonates having the optimum properties. This is because fractionation at 160°C at 5 mm. Hg. of the total alkylate product yielded when this mole ratio is employed yields a bottoms alkylate which contains less than 25 weight percent diphenylalkanes and is therefore suitable for sulfonation without further treatment.

The alkylate compositions derived from the alkylate bottoms in the manner described comprise at least 35 weight percent di-n-alkaryl compounds, less than 40 weight percent diphenylalkanes and the balance consists essentially of naphthalene compounds and tetralin compounds. The alkyl substituents of the di-n-alkaryl compounds contain from eight to 18 carbon atoms, and at least 95 percent of the alkyl substituents are bonded through a secondary carbon atom to the aromatic portion of the molecule. From 20 to 60 mole percent of the di-n-alkaryl compounds are meta disubstituted, the balance being paradisubstituted.

The alkylate can be further characterized as boiling above 160°C at 5 mm. Hg. and as having a molecular weight exceeding 325. Other properties of preferred alkylate compositions which contain at least 50 weight percent di-n-alkaryl compounds and not exceeding 25 weight percent diphenylalkane compounds are as follows:

Viscosity at	
210°F, in centistokes	4-7
100°F, in centistokes	25-45
0°F, in centistokes	1000-2500
Viscosity Index	85-110
Pour Point	Less than -50°F
Flash Point	Exceeds 350°F

Within the foregoing broad definition and characterization of these alkylates, the alkylate compositions which are preferred for use in preparing the novel sulfonates of the present invention are those in which the alkyl substituents of di-n-alkaryl compounds contain from 10 to 16 carbon atoms. It is further preferred that the alkylates contain from 60 to 75 weight percent di-n-alkaryl compounds, less than 16 weight percent diphenylalkanes, have an average molecular weight of from about 375 to about 475, and a flash point exceeding 400°F.

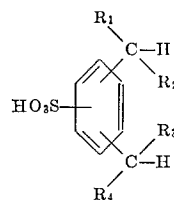
The sulfonation of the fractionated bottoms alkylate to yield oil soluble sulfonic acid compositions can be carried out by any one of a number of conventional methods using either oleum, SO₃, mixtures of SO₃ and SO₂ or chlorosulfonic acid. The employment of oleum for the sulfonation procedure is preferred. Additional details with respect to a suitable method for sulfonating these alkylate stocks will be set forth in the specific examples appearing hereinafter.

The oil soluble sulfonic acids can be subjected to neutralization or overbasing procedures heretofore known to the art, such as those disclosed in U.S. Pat. No. 2,861,951 to Carlyle, U.S. Pat. No. 3,150,089 to Hunt, and U.S. Pat. No. 3,150,088 to Hunt et al. Although these patents described processes for simulta-

neously neutralizing the oil soluble sulfonic acid compositions and dispersing therein metal hydroxides, metal carbonates or metal alkoxide complexes to impart reserve basicity to the product compositions, the present invention also comprehends the mere neutralization of the sulfonic acid compositions to yield neutral sulfonates. Such neutral compositions, by reason of their relatively low viscosity and desirable rust inhibiting and emulsion suppressing properties, are valuable stocks for blending with overbased sulfonate additive compositions which, though possessing good peptizing ability and high basicity, are much more viscous than desirable, or lack the specific rust inhibiting and water demulsifying characteristics for a given application.

The sulfonic acid compositions derived from the bottoms alkylate have an average combining weight of at least 400, and preferably from about 430 to about 525.

The acids are believed to be substantially entirely monosulfonated with the sulfonic acid group attached directly to the aryl nucleus. In the case of the di-n-alkylbenzene sulfonic acids derived from benzene, the preferred aromatic starting material, the acids can be represented by the structural formula



where R₁ and R₃ are straight-chain alkyl groups of one to eight carbon atoms, and R₂ and R₄ are straight chain alkyl groups of one to nine carbon atoms. Preferably the sum of the carbon atoms in R₁ and R₂, and the sum of the carbon atoms in R₃ and R₄ are each from nine to 15 carbon atoms.

The novel oil soluble metal sulfonate compositions derived from the sulfonic acid compositions can be either neutral or overbased compositions. The sulfonates can be the salts of substantially any neutralizing metal, as well as of ammonia and amines, such as ethylene diamine. The preferred sulfonates are barium, calcium and magnesium salts. The compositions contain at least 20 weight percent, more suitably at least 35 weight percent, and preferably at least 50 weight percent of the di-n-alkaryl metal sulfonates. The structural character of the metal sulfonates can be defined by reference to the sulfonic acids and alkylates from which they are made. The sulfonate compositions are further preferably characterized in having a viscosity at 210°F which does not exceed 750 centistokes.

In order to illustrate further the details of the preparation and the nature of the compositions of the present invention, the following specific examples are given. All parts referred to in the examples are parts by weight unless otherwise indicated.

EXAMPLE 1

This example primarily illustrates the alkylation step used for preparing an alkylate product which is suitable for making high quality biodegradable detergent as well as the compositions of the present invention.

A kerosene fraction was segregated by the urea adduction to yield a mixture of n-paraffins having the following composition:

n-paraffins	Weight Percent
C ₉	0.8
C ₁₀	4.0
C ₁₁	9.5
C ₁₂	17.2
C ₁₃	22.6
C ₁₄	24.2
C ₁₅	14.5
C ₁₆	2.8
Slightly Branched C ₁₁ -C ₁₅	3.5

This paraffinic mixture was then subjected to chlorination, to yield a mixture in which 22.3 mole percent of the n-paraffins were converted to chloroparaffins, 90 percent of which were monochlorinated.

Nine hundred thirty-seven parts of this chlorination reaction product was then placed in a vessel equipped with a stirrer and thermometer, along with 850 parts (10.9 mole equivalents) of benzene. The weight of the chlorinated n-paraffins present in the charge was 238 parts (1.1 mole equivalents). The amount of aluminum chloride catalyst used was 5.5 percent based on the weight of chloroparaffins present.

After complete addition of the chlorinated product, the temperature was raised to 45°C whereupon nitrogen gas was blown through the reaction mixture and the reaction mixture was poststirred for about 45 minutes. Purging with nitrogen was continued until about 89.7 percent of the chlorinated material was accounted for as HCl. The alkylate was allowed to cool to room temperature and permitted to stand until the sludge content thereof had completely settled. The alkylate was then separated from the sludge and was washed with sulfuric acid and base.

The washed crude alkylate fraction was then fractionated as follows:

Benzene—Up to a vapor temperature of 130°C at atmospheric pressure
n-paraffins—Up to 155°C at 20 mm. Hg.
Detergent alkylate—153°-225°C at 20 mm. Hg.
Bottoms alkylate—Material boiling above 225°C at 20 mm. Hg.

EXAMPLE 2

In determining the composition of the bottoms alkylate in order to better understand the mechanism responsible for a portion of the alkylate being easily sulfonatable to produce the oil soluble sulfonates herein described, a series of alkylation reactions was performed in which the mole ratio of benzene to chloroparaffins employed was decreased gradually from 10:1 down to 1:1. In each case, the detergent alkylate-bottoms alkylate cut point was 161°C at 5 mm. Hg. The results of these alkylations in terms of the mole ratio of reactants employed, the grams of bottoms alkylate yielded, and the analysis of the bottoms alkylate for dialkylbenzenes and diphenylalkanes are set forth in Table 1.

TABLE I

Mole Ratio Benzene/RCI	Grams of Bottoms Produced	Composition, Diphenyl- alkanes	Weight Percent Dialkylbenzenes and Others
10:1	8	60	40
8:1	9	55	45
6:1	19	46	54
4:1	28	33	67
3:1	37	24	76
2:1	46	17	83
1:1	73	6	94

EXAMPLE 3

This example is illustrative of an alkylation reaction carried out using a 3:1 mole ratio of benzene to chloroparaffins as the alkylation reactant ratio. 5,000 grams of chlorinated C₁₁ — C₁₄ n-paraffins (4.43 weight percent chlorine) and 1,541 grams of benzene were weighed into a three-necked flask equipped with a stirrer, thermometer and reflux condenser. Heat was applied with a heating mantle to bring the temperature in the flask to 65°C. The entire aluminum chloride catalyst in the amount of 50 grams was then added at one time while the contents of the flask were stirred. The mixture was stirred for 1½ hours following addition of the catalyst while maintaining the temperature at 65°C. The crude alkylate was then settled in a separatory funnel for one hour and the catalyst sludge layer (141 grams) was removed from the bottom of the funnel. The alkylate was then washed successively with 540 grams of concentrated sulfuric acid and 2,000 ml. of 5 percent sodium hydroxide. The excess benzene was then distilled from the mixture at 1 atmosphere pressure to a pot temperature of 235°C and a vapor temperature of 145°C. The benzene-free crude alkylate was then fractionated to yield the following cuts:

Excess n-paraffins	I.B.P. to 155°C at 20 mm. Hg.
Detergent alkylate, 1st cut	155°-167°C at 20 mm. Hg.
Detergent alkylate, 2nd cut	85°-161°C at 5 mm. Hg.
Bottoms alkylate	Over 161°C at 5 mm. Hg.

The yields of the alkylates and excess normal paraffins derived from the benzene-free total alkylate were as follows:

Fraction	Weight, grams	Mole Percent of paraffins consumed
Excess n-paraffins	3863	—
Detergent alkylate	1033	75.4
Bottoms alkylate	198	8.1

The bottoms alkylate yielded was 19.1 weight percent of the total alkylate produced.

EXAMPLE 4

The bottoms alkylate produced in Example 3 was subjected to distillation to remove 20 volume percent of the total bottoms alkylate. The topped alkylate product was then analyzed by mass spectrometer as follows:

Component	Weight Percent
Dialkylbenzenes	72.7
Alkyl naphthalenes	10.0
Alkyl tetralins and indanes	12.1
Diphenylalkanes	5.2

The fractionated bottoms alkylate obtained by removing the light ends to the extent of 20 volume percent were sulfonated and neutralized and subjected to overbasing using the procedure described in Carlyle U.S. Pat. No. 2,861,951. The overbased sulfonate additive was bright and fluid, and when added to an oil base, remained stable over extended periods of time.

EXAMPLE 5

This example is provided to demonstrate the manner in which the fractionated alkylate bottoms products can be used to prepare oil soluble sulfonic acids which can be treated by known procedures to prepare the novel overbased sulfonate compositions of the present

invention for use in lubricating oils, Diesel oils and the like in the manner hereinbefore described.

One hundred fifty grams of alkylate bottoms prepared as described in Example 3 and topped by removing 20 volume percent of the light ends therefrom as described in Example 4 were placed in a 1-liter creased, three-necked flask and diluted with 121 grams of 100 pale oil. The diluted alkylate was then sulfonated at a temperature of 50° to 55°C using 150 grams of reagent grade oleum (about 20 weight percent SO₃) added over a period of 15 minutes to the reaction flask.

The crude sulfonation mass was then gravity settled overnight at 50°C to remove the bulk of the acid sludge from the crude sulfonic acid-oil layer by a primary sludge split. The crude acid-oil layer was diluted with 1.6 volumes of naphtha per volume of crude acid-oil. A secondary sludge split was then taken after gravity settling at ambient temperature for 24 hours. The naphtha diluted acid-oil layer was further purified by treating with calcium hydroxide and purging with nitrogen. The 355 grams of purified sulfonic acid as thus prepared analyzed as follows:

Total Acid, meq./gram	0.564
Sulfonic Acid, meq./gram	0.547
Weight Percent Nonvolatiles	44.3
Weight Percent Sulfonic Acid	24.8

To 175 grams of purified sulfonic acid solution was charged 60 grams of 2-methoxy ethanol-barium oxide complex. The base number of the complex was 208 as determined by the acetic acid titration method and described in Analytical Chemistry, Vol. 23, No. 2, February, 1951, and Vol. 24, No. 3, Mar. 1952, p. 519. The barium complex was added over a period of about 5 minutes before mechanically agitating the mixture. The temperature of the mixture was then adjusted to 45° to 50°C and the reaction mass was blown with gaseous CO₂ until acidic to α -naphthol benzene indicator. After carbonation, the volatile materials were removed overhead to a pot temperature of 150°C, and the reaction product was then stripped with CO₂ at 150 to 155°C for about 10 minutes. The resultant overbased additive product at ambient temperature was fluid, considered bright, and was not filtered. The material had the following analysis:

Base number (by acetic acid method)	71
Weight percent barium sulfonate	50.3
Combining weight (as barium)	523

The product was oil soluble and, when treated with small amounts of conventional antifoam and antioxidant additives, demonstrated good storage stability and antifoam properties. The product had good compatibility with brightstock and in standard engine tests of lubricating oils to which it was added, yielded good results.

EXAMPLE 6

A number of samples derived from alkylate bottoms prepared in the manner described in Example 3 were topped to differing extents so as to produce sulfonation stocks having varying contents of diphenylalkane compounds as more specifically indicated in Table II hereinafter. These sulfonation stocks were then subjected to sulfonation after blending 60 parts of the fractionated bottoms samples with 40 parts of 100 pale oil. The sulfonation was carried out at 160°F using a volumetric ratio of 0.75:1 oleum to alkylate bottoms.

After sulfonation, the sulfonic acid was purified by the lime treatment as described in Example 5. The sulfonated samples were each then subjected to neutralization and overbasing using methanolic barium oxide as described in Carlyle U.S. Pat. No. 2,861,951. The overbased sulfonate compositions thus produced were characterized by the activities and base numbers (as determined by the acetic acid method) set forth in Table II. The sulfonates were subjected to BS & W testing and the results obtained are set forth in Table II. In the BS & W test, a blend of the barium sulfonate and petroleum naphtha in an equal volumetric proportion is centrifuged for 10 minutes at 1,500 RPM. The sediment removed by centrifugation is weighed and evaluated as a weight percent of the entire blend.

TABLE II

Sample*	1	2	3	4	5	6	7
Weight percent diphenylalkanes	9.8	10.5	10.2	16.6	23.8	32.1	25.7
Sulfonation:							
Yield, lbs. RSO ₃ H/lb. bottoms	96.2	86.4	78.9	71.9	52.6	63.2	54.6
Molecular weight as Na salt	461	454	450	486	450	461	477
Percent RSO ₃ H	50.4	46.9	44.5	45.4	38.5	43.6	40.1
Barium sulfonate analysis:							
Percent active	48.0	46.7	51.0	48.0	40.9	43.0	41.9
Base number	62.4	62.1	28.0	63.1	55.2	54.9	49.0
BS & W	0.02	0.016	0.020	0.06	0.16	0.10	0.3

*The alkylates of Samples 1-3 were made using a 3:1 mole ratio of benzene to chloroparaffins; the alkylate of Sample 4 was made using a 6:1 ratio of benzene to chloroparaffins and the alkylates of Samples 5-7 were made using a 9:1 ratio of benzene to chloroparaffins.

A frequent industrial specification for the BS & W test is 0.02 weight percent maximum. It will thus be perceived in referring to Table II that the diphenylalkane content of the bottoms is preferably maintained below about 16 percent for the purpose of yielding an overbased barium sulfonate composition meeting the usual specification in this test.

EXAMPLE 7

This example illustrates the properties of typical alkylates suitable for use in preparing the sulfonate compositions of this invention.

A bottoms alkylate fraction was prepared by the alkylation process hereinbefore described using a benzene to chloroparaffin ratio of 3:1 and employing a relatively narrow fraction of chlorinated paraffin hydrocarbons having chain lengths of from 10 to 12 carbon atoms. Three portions of the bottoms alkylate obtained after separating the light detergent alkylate therefrom were subjected to topping to various degrees to yield alkylate fractions having the following properties and weight percent analyses by mass spectrometer.

Sample	1	2	3
Cut point in Topping, °F at 5 mm.	452	458	467
Hg.	72	66	60
Volume Percent Bottoms Alkylate	15.9	16.3	16.8
Tetralins, Weight Percent	55.7	55.0	57.2
Dialkylbenzenes, Weight Percent	21.4	21.8	18.9
Diphenylalkanes	7.0	7.3	7.0
Naphthalenes			
Viscosity, cs. at 210°F.	5.65	5.93	6.12

at 100°F	37.65	40.33	42.91
at 0°F	1610	1810	1990
at -40°F	25,340	29,900	34,250
Viscosity Index	96	98	95
Pour Point	-70	-70	-70
Flash Point	400	400	400

EXAMPLE 8

The fractionated bottoms alkylate samples of Example 7 were sulfonated in 100 pale oil with 20 percent oleum. Three portions of Sample 2 were subjected to sulfonation on different quantitative scales as shown hereinafter in Table III. The sulfonation were carried out at temperatures of between 50° and 60°C.

Purification of the sulfonated samples was accomplished by treating with calcium hydroxide followed by nitrogen degassing. The conditions obtaining during sulfonation and purification, and the results of analysis of the purified sulfonic acid product are given in Table III.

TABLE III

Sample	1	2A	2B	2C	3
Molecular weight		414	414	414	418
Sulfonation:					
Alkylate, g.	100	1,500	150.0	150.0	100
100 pale oil, g.	80.5	1,210	121.0	121.0	80.5
Oleum, g.	140.0	2,250	225.0	255.0	140.0
Weight ratio of oleum/alkylate	1.4/1	1.5/1	1.5/1	1.7/1	1.4/1
Primary sludge, g.	122.0	1,885	189.4	214.3	115.0
Dilution, hexane, ml.	344	5,025	514	518	342
Total sludge recovered, g.	138.6	2,180.6	214.3	243.6	136.5
Weight ratio, total sludge/oleum	0.99	0.97	0.95	0.96	0.98
Sulfonic acid solution, g.	383.3	5,970	620.0	670.2	395.0
Total acid, meq./g.	0.768	0.814	0.812	0.918	0.814
Sulfonic acid, meq./g.	0.527	0.522	0.539	0.557	0.532
Combining weight (RSO ₃ H)	444	444	436	439	435
Acid ratio, less SO ₂ *	5.1	6.2	5.7	7.3	6.0
Yield, g. RSO ₃ H/g. alkylate	0.90	0.93	0.97	0.99	0.91
Purification:					
Sulfonic acid solution, g.	343.5	5,682	377.5	369.2	118.5
CA(OH) ₂ , g.	4.5	91.9	5.7	7.3	1.9
Purified acid, g.	347.5	5,389	391.3	330.0	165.3
Total acid, meq./g.	0.540	0.556	0.524	0.619	0.391
Sulfonic acid, meq./g.	0.517	0.546	0.500	0.613	0.379
Acid ratio	0.49	0.22	0.54	Nil	0.36
Weight percent nonvolatiles	44.6	45.8	40.4	48.0	31.2

* Grams inorganic acid as H₂SO₄ per 100 grams RSO₃H.

EXAMPLE 9

Overbased barium sulfonate compositions were prepared from the purified sulfonic acid compositions produced in Example 8 using methanolic barium oxide in the manner described in Carlyle U.S. Pat. No. 2,861,951 to neutralize and overbase the sulfonic acid compositions while mixed with 100 pale oil. The barium hydroxide in the compositions was converted to the carbonate by blowing with CO₂. The amount of the materials used in the overbasing procedure and the properties of the product sulfonates are set forth in Table IV.

TABLE IV

Sulfonic acid sample	1	2a	2b	2c	3
Sulfonic acid, g.	278.8	4,900	338.5	269.5	136.2
100 pale oil, g.	11.3	153.0	15.0	18.2	3.9
Methanol-BaO, g.	*171.0	*3,021	209.5	204.5	63.8
Yield of overbased Ba sulfonate, g.	164.8	2,924	188.2	181.8	57.4
Sulfonate base number	74	65	75	78	78
Percent active (as Ba)	44.2	46.8	45.3	46.1	45.2

* In these overbasing runs, the methanolic barium oxide employed had a base number of 118; in the other runs the methanolic barium oxide used had a base number of 112.

All of the sulfonates described in Table IV were bright and fluid and filtration was not required. Blends of the sulfonates with oil base stocks, including brightstock, remained stable and bright after 90 days.

The sample 2a sulfonate was used in preparing a lubricating oil composition of SAE 30 viscosity which contained the following:

Additives

5 percent by weight of the barium carbonate-containing sulfonate composition prepared from Sample 2a above

0.07 weight percent zinc present as zinc dithiophosphate oxidation inhibitor

30 p.p.m. silicone oil foam inhibitor

Mineral Oil Base

31.6 percent by weight neutral 170 pale oil

29.5 percent by weight neutral 400 pale oil

31.6 percent by weight 95 viscosity index brightstock

The SAE 30 lubricating oil composition made up as described was evaluated in a Caterpillar S-1 engine test. The Caterpillar test was run under identical conditions on an SAE 30 lubricating oil which contained a heretofore widely employed sulfonate composition overbased with barium carbonate, and prepared in accordance with previously employed procedures. The comparative data obtained from the Caterpillar S-1 test are set forth in Table V. The duration of the test was 480 hours.

TABLE V

	SAE 30 Lubricating Oil by Invention	Conventional SAE 30 Lubricating Oil
Rating after 480 hours	Pass	Pass
Lacquer in top groove	Trace	Trace
Top groove filling, % volume	12	5
Lacquer of first land	Trace	Trace
Lacquer in second groove	None	None
Lacquer below second groove	Trace	Trace

The Caterpillar test results set forth in Table V indicate that the overbased sulfonate compositions of the present invention perform comparably in engine tests to sulfonate compositions derived from a different type of alkylate stock and previously widely used commercially as additives for lubricating oils.

EXAMPLE 10

A bottoms alkylate was prepared in the manner described in Example 1, but employing a 3:1 mole ratio of benzene to an alkylation reagent consisting essentially of a relatively narrow fraction of chloroparaffins of from 12 to 14 carbon atoms in chain length. The bottoms alkylate thus prepared was topped to remove 20 volume percent of the total bottoms alkylate. The cut point employed in topping the total alkylate bottoms was 235°C at 5 mm. Hg. The fraction remaining after topping was analyzed by mass spectrometer as follows:

Dialkylbenzenes	65.8 volume percent
Diphenylalkanes	22.3 volume percent
Naphthalenes	12.0 volume percent

Infrared data indicated that the dialkylbenzenes present were about 60 mole percent para disubstituted and 40 mole percent meta disubstituted. The average molecular weight of the topped alkylate as determined by osmometer was 440.

Additional properties of the topped alkylate composition were determined as follows:

Viscosity, cs.	5.95
210°F	39.57
100°F	1647
0°F	23,000
-40°F	103
Viscosity Index	455
Flash Point, °F	-80°F
Pour Point	

The topped alkylate bottoms having the composition set forth above were subjected to sulfonation with different amounts of 20 percent oleum. The sulfonation was carried out in 100 pale oil at a temperature of 50 to 55°C. The oleum used for sulfonation was reagent grade containing 20 weight percent SO₃ and the time of addition of the oleum to the pale oil-sulfonic acid mixture varied from about 5 to about 25 minutes.

After gravity settling of the sulfonic acid product, a primary sludge split was taken. The crude acid-oil was diluted with 1.6 volumes of naphtha per volume of crude acid-oil. A secondary sludge split was then taken after gravity settling at ambient temperature for a minimum of 24 hours.

Purification of the sulfonate was accomplished using calcium hydroxide followed by nitrogen degassing. During the lime treating, external cooling was not required, and in some cases, the reactions were warmed to about 30°C to insure purification. The quantities of materials used in the sulfonation, solvent dilution and purification by lime treating are set forth in Table VI.

Properties and amounts of the products yielded in the various steps of the sulfonation procedure are also set forth in this table.

TABLE VI

Sample.....	1	2	3	4	5	6
Sulfonation charge:						
Alkylate, g.....	150.0	150.0	1,500	1,500	1,500	150.0
100 pale oil, g.....	121.0	121.0	1,210	1,210	1,210	121.0
Oleum, g.....	150.0	180.0	2,100	2,100	2,100	270.0
Weight ratio, oleum/alkylate.....	1.0/1	1.2/1	1.4/1	1.4/1	1.4/1	1.8/1
Primary sludge, g.....	125.3	150.5	1,708	1,719	1,848	232.2
Dilution, Sp. naphtha, ml.....	495.0	500.0	5,080	5,100	5,100	505.0
Total sludge recovered, g.....	142.9	173.2	1,916	1,916	1,934	251.5
Sulfonic acid solution, g.....	619.5	621.8	6,357	6,374	6,396	631.7
Total acid, meq./g.....	0.537	0.622	0.765	0.765	0.765	0.765
Sulfonic acid, meq./g.....	0.454	0.500	0.512	0.512	0.512	0.557
Combining weight (RSO ₃ H).....	460	465	470	470	470	463
Yield, g. RSO ₃ H/g. alkylate.....	0.88	0.97	5.1	5.1	5.1	1.09
Purification:						
Sulfonic acid solution, g.....	289.5	296.6	5,920	6,374	6,396	361.5
Ca(OH) ₂ , g.....	1.3	3.0	83.5	90.0	90.0	4.0
Purified acid, g.....	355.4	320.1	5,441	*11,808	11,808	400.4
Total acid, meq./g.....	0.388	0.488	0.557	0.541	0.541	0.517
Sulfonic acid, meq./g.....	0.388	0.480	0.538	0.529	0.529	0.497
Acid ratio, less SO ₂	Nil	0.17	0.37	0.25	0.25	0.43
Weight percent nonvolatiles.....	35.7	40.9	45.6	45.0	45.0	39.2

*After lime purification, Samples 4 and 5 were composited for analysis and the analysis of the composite then appears in lower portion of the column under Sample 4.

The sulfonic acid prepared by sulfonating Sample 3 in Table VI was subjected to neutralization and overbasing using methanolic barium hydroxide. 5,000 grams of the sulfonic acid was mixed with 218 grams of 100 pale oil and treated with 3,307 grams of the methanolic barium hydroxide in accordance with the process conditions described in U.S. Pat. No. 2,861,951. The product overbased sulfonate dispersion was stripped with carbon dioxide gas for 45 minutes at 150° to 155°C. There were isolated from the reaction product, 3,097 grams of a bright, fluid, overbased sulfonate dispersion which had the following analysis:

Base Number	73
Weight percent active	46.8
Combining Weight (as Ba)	538
Weight percent Ca	0.04
Weight percent Ba	15.3
Weight percent S	2.68
Viscosity 210°F, centistokes	51.78
Flash, COC, °F	410
A.S.T.M. color	6.5

Storage compatability and foaming properties of the overbased sulfonate dispersion were determined on a blend consisting of 4.8 weight percent of the overbased

sulfonate, 2.25 weight percent Oronite 260 and 3 p.p.m. Dow-Corning 200 silicone oil having a viscosity of 500 centistokes, all in SAE 30 weight lubricating oil base stock. After 90 days in storage, the blends remained bright at ambient temperature and at 50°C. Ambient temperature, as here used, and as used throughout this specification refers to a temperature of from 20°C to 35°C.

In bright stock storage compatibility tests, 16 weight percent of the overbased barium sulfonate was blended with bright stock. After 90 days at ambient temperature and at 50°C, the bright stock blends remained bright.

EXAMPLE 11

This example illustrates the versatility of the topped bottoms alkylate prepared in accordance with this invention, insofar as is concerned its suitability as a sulfonation stock for making various types of overbased, oil soluble metal sulfonate compositions by different currently known overbasing procedures.

A portion of the purified sulfonic acid derived from the composite of crude sulfonic acids made from Samples 4 and 5 in Example 10 (see footnotes to Table VI)

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was subjected to neutralization and overbasing in accordance with the process described in Hunt et al. U.S. Pat. No. 3,150,088 to provide a highly basic calcium sulfonate dispersion having a bright, clear appearance, good stability and a base number of 292. The viscosity of this composition at 210°F was 90 centistokes. This sulfonate product compared well with conventional oil soluble sulfonate compositions prepared from a polydodecylbenzene alkylate made by reacting dodecene with benzene to obtain a bottoms alkylate, sulfonating and then using the identical overbasing procedure as here used and as described in U.S. Pat. No. 3,150,088.

A second portion of the same purified sulfonic acid used to prepare the overbased calcium sulfonate composition was subjected to the overbasing procedure described in Hunt et al U.S. Pat. No. 3,150,089 to yield a magnesium sulfonate having a base number of 296 and a viscosity at 219°F of 255 centistokes. The magnesium sulfonate composition performed satisfactorily in engine tests of the type hereinbefore described.

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EXAMPLE 12

This example illustrates the superior rust inhibiting and water demulsibility qualities of the overbased oil

soluble sulfonates of this invention, as compared to oil soluble sulfonate additives derived from alkylates prepared using propylene tetramer as alkylating agents to produce dodecylbenzene alkylates.

Overbased barium sulfonate compositions prepared in the manner described in Example 10, Sample 3, and in Example 9, Sample 2a, were added to a turbine oil base stock having an overall viscosity of 160 S.S.U. at 100°C. Other conventional additives were also added to the base stock, and the weight percent of the additives included in the turbine oil is indicated in Table VII.

For purposes of comparison a postdodecylbenzene was sulfonated, neutralized and overbased with methanolic barium oxide to produce an overbased barium sulfonate having a base number of 70, and was also tested for rust inhibiting and water demulsibility properties. The particular composition of the turbine oil blends tested and the results of the test are set forth in Table VII.

TABLE VII

Run No.	1	2	3
Additives, Weight %			
Anti-oxidants	0.45	0.45	0.43
Sulfonate A	0.12	—	—
Sulfonate B	—	0.12	—
Sulfonate C	—	—	0.10
Test Results			
Rust Test*	Pass	Fail	Pass
Water Emulsion**	40-40-0-20	29-0-51-60	40-39-1-20

* ASTM D-665 using synthetic sea water.

** ASTM Water Emulsion Test D-1401 conducted at 130°F. The four values reported are, in order, ml. in oil layer, ml. in water layer, ml. in cuff or emulsion, time of standing in minutes.

Sulfonate A = overbased barium sulfonate derived from Sample 2a of Table IV in Example 9; base number 65, percent active 46.8.

Sulfonate B = overbased barium sulfonate derived from postdodecylbenzene; base number 70.

Sulfonate C = overbased barium sulfonate derived from Sample 3 in Example 10; base number 74, percent active 46.8.

In referring to Table VII, it will be perceived that the overbased sulfonates produced in accordance with the present invention are clearly superior in their rust inhibiting and water demulsification properties to sulfonates prepared from conventional, previously used benzene alkylate type sulfonation stocks.

Although the sulfonates tested had quantitative properties which were quite similar, the sulfonates prepared in accordance with the present invention had considerably lower viscosities than those derived from the previously used alkylate sulfonation stocks.

EXAMPLE 13

Two alkylation reactions were carried out as described in Example 3 using in each case chlorinated n-paraffins containing from 10 to 13 carbon atoms. The mole ratio employed in one alkylation was 0.25:1 and in the other 0.5:1 (benzene to chloroparaffin). About 2,000 grams of the chlorinated n-paraffins were used in each alkylation run and in each case contained 4.8 weight percent chlorine. The alkylate bottoms were segregated by distillation and constituted that portion distilling above 196°C at 10 mm. Hg. These two bottoms alkylates had the following compositions as determined by mass spectrometer:

	Reactant Mole Ratio Employed	
	0.25/1	0.50/1
Dialkylbenzenes, volume percent	72.3	76.0
Diphenylalkanes, volume percent	9.7	2.6
Tetralins and Indanes, volume percent	8.9	13.2

Naphthalenes and Other Components, volume percent	9.7	8.3
Molecular Weight	422	398

The alkylates thus prepared were sulfonated using the general procedure described in Example 5. The alkylate prepared using a reactant ratio of 0.25:1 yielded 0.90 grams of sulfonic acid per gram of the alkylate for a percent sulfonated yield of 77.4 percent and the combining weight of this sulfonic acid was 496. The alkylate prepared using a reactant ratio of 0.5:1 yielded 1.17 grams of acid per gram of alkylate—a yield of 98.3 percent.

From the two sulfonic acids thus prepared, overbased calcium sulfonate compositions were prepared as described in Example 11. The overbased calcium sulfonate derived from alkylate prepared using a 0.5 to 1 reactant mole ratio had a calcium sulfonate base number of 266, and a viscosity at 210°F of 73.7 centistokes. The overbased calcium sulfonate derived from alkylate prepared using a 0.25 to 1 reactant mole ratio had a base number of 338, and a viscosity at 210°F of 486 centistokes.

EXAMPLE 14

A bottoms alkylate was prepared in the general manner described in Example 1, but employing a benzene to chloroparaffin ratio of 10:1. The chlorinated paraffin hydrocarbon used included compounds in which the chain lengths ranged from 12 to 16 carbon atoms. The cut point used in topping the bottoms alkylate after removal of the light detergent alkylate therefrom was 450°F at 5 mm. Hg. The mass spectrometer analysis of the portion remaining after topping was as follows:

Dialkylbenzenes	43.4 volume percent
Diphenylalkanes	31.4 volume percent
Tetralins and Indanes	17.0 volume percent
Naphthalenes	1.1 volume percent
Other components	8.2 volume percent

The fractionated bottoms were sulfonated in hexane with 20 percent oleum at an oleum level of 1.7 to 1. The sulfonation was carried out at a temperature between 50°C and 60°C. The following data was recorded concerning the sulfonation:

Sulfonation charge:	
alkylate	100 grams
oleum	170 grams
hexane*	100 grams
Ratio of total sludge removed to oleum charged, by weight	1.31
Hexane - RSO ₃ H	266.5 grams
Total acid	0.40 milliequivalents/gram
Sulfonic acid	0.30 milliequivalents/gram
Yield, grams of RSO ₃ H per gram of alkylate**	0.38
*Sulfonation carried out in 50 ml. hexane; 102 ml. hexane added after sulfonation	
**Combining weight of 480 for RSO ₃ H was assumed	

EXAMPLE 15

A sulfonic acid prepared as described in Example 13 was purified by treating with Ca(OH)₂ followed by nitrogen degassing. The purified sulfonic acid had the following analysis:

Total acid, milliequivalents/gram	0.296
Sulfonic acid, milliequivalents/gram	0.326
Weight percent nonvolatiles	18.9

From the purified sulfonic acid, overbased barium sulfonate compositions were prepared as described in Example 9. The amount of the materials used in the over-basing procedure and the properties of the product sulfonates produced were as follows:

Sulfonic acid	350 grams
100 Pale Oil	47.6 grams
Methanolic Barium Oxide	131 grams
Yield of Overbased Sulfonate	136.3 grams
	(117 base number)
Sulfonate Base Number	72
Weight Percent Active (as Ba)	46

SULFONATES FROM "MIXED ALKYLATES"

In this aspect of the present invention, novel oil soluble metal sulfonates are prepared from alkylate compositions containing a predominant amount of dialkaryl compounds in which one of the alkyl substituents is branched and the other linear or straight chain. The mixed alkylate from which the oil soluble metal sulfonates are derived can be prepared by either of two procedures.

In one of the procedures, detergent alkylate produced by the method described in U.S. Pat. No. 3,316,294 and as previously outlined herein, is subjected to a further alkylation reaction using a propylene tetramer of the type which has conventionally been employed to prepare polydodecylbenzene alkylates in accordance with known procedures. The propylene tetramer can be prepared by polymerizing propylene over a phosphoric acid catalyst, and typically has an average molecular weight of from about 165 to about 175, a bromine number of from about 95 to about 110, and a peroxide number of from about 1 to about 5. The detergent alkylate will generally contain in excess of 90 weight percent mono-n-alkaryl compounds.

The further alkylation of the detergent alkylate with propylene tetramer is carried out using alkylation procedures well understood in the art. These may be generally characterized as including the use of a Friedel-Crafts catalyst, preferably $AlCl_3$, with HCl or water added as a catalyst promoter. The temperature employed is from about 50°C to about 65°C, and preferably from 55°C to 60°C.

The crude alkylate produced by this alkylation step is then fractionated to yield a bottoms mixed alkylate containing at least 75 mole percent dialkaryl compounds and having an average molecular weight of from about 375 to 475. The cut point used in the fractionation to obtain the bottoms mixed alkylate is preferably from about 180°C to about 200°C at 5 mm. Hg. The dialkaryl compounds in the bottoms mixed alkylate contain a majority of disubstituted compounds in which one of the alkyl substituents is from propylene tetramer and highly branched, and the other alkyl substituent is linear or straight chain.

The second procedure which we have found can be employed to produce a mixed alkylate composition containing dialkaryl compounds of the described character comprises using a haloparaffin alkylating agent of the type employed in the detergent alkylate process of U.S. Pat. No. 3,316,294 to further alkylate a monoalkaryl alkylate produced by initially alkylating an aromatic compound with a propylene tetramer of the character described above. A monoalkaryl alkylate of this type consists essentially of monoalkaryl compounds in which the alkyl substituents are highly branched and contain from nine to 16 carbon atoms. Over 70 mole

percent of the alkaryl compounds will be substituted by an alkyl group containing from 11 to 13 carbon atoms. Preparation of an alkylate of this type for use as a charge stock in preparing conventional detergents is well understood in the art and details of the reaction conditions employed in this well understood and conventional preparation need not be set forth in this application.

The reaction of the haloparaffin alkylating agent (having the properties hereinbefore described) with monoalkaryl compound-containing alkylate is effected in substantially the same manner as is characteristic of the alkylation process used in preparing biodegradable detergent alkylate as previously described herein. The product of this alkylation reaction is fractionated to yield a fraction boiling above from about 180°C to 200°C at 5 mm. Hg. and containing at least 75 mole percent dialkaryl compounds in which the alkyl substituents are branched and linear.

The higher boiling fraction of mixed alkylate prepared by either of the procedures described above is subjected to the sulfonation, neutralization and over-basing procedures hereinbefore described to produce novel oil soluble metal sulfonate compositions. The sulfonates can be the salts of substantially any base metal as well as of ammonia and amines. The compositions contain at least 20 weight percent and preferably at least 40 weight percent of the mixed alkylate metal sulfonates. The structural character of the metal sulfonates can be defined by reference to the dialkaryl compounds from which they are made.

Within the foregoing broad characterization of the mixed alkylate sulfonates of the present invention, it is preferred that the differences in the number of carbon atoms in the alkyl substituents on the aryl moiety does not exceed 4. That is, the number of carbon atoms in the branched chain alkyl group attached to the aryl moiety as compared to the number of carbon atoms in the straight chain alkyl group attached to the aryl moiety should not be different by more than 4. The mixed alkylate sulfonate compositions are further preferably characterized in having a viscosity at 210°F which does not exceed 750 centistokes.

The following examples will further illustrate the oil soluble metal sulfonates prepared by the above described two processes.

EXAMPLE 16

In this example, an alkylate consisting essentially of monoalkylbenzene compound produced by alkylating benzene with a propylene tetramer was subjected to further alkylation, using a chlorination product like that described in Example 1 as the alkylating agent. The monoalkylbenzene alkylate had an average molecular weight of 239, a specific gravity of 0.8723 and substantially all of the alkyl group substituents of the aromatic nucleus of the alkylbenzene compounds therein were highly branched. The distribution of alkyl substituents of the monoalkyl benzene compounds was indicated by mass spectrometer to be

Alkyl Group	Mole Percent
C ₉	0.81
C ₁₀	1.69
C ₁₁	24.04
C ₁₂	51.68
C ₁₃	13.84
C ₁₄	4.81
C ₁₅	2.34
C ₁₆	0.79

The boiling range of the alkylate by ASTM D-86 was

I.B.P.	350°F
5%	356°F
10%	358°F
50%	367°F
90%	390°F
95%	404°F
E.P.	416°F

Preparation of a detergent alkylate of this type is well understood in the art and involves contacting benzene with a propylene tetramer prepared by polymerizing propylene over a phosphoric acid catalyst. The tetramer alkylating agent thus produced typically has an average molecular weight of from 165 to about 175, a bromine number of from about 95 to about 110, a peroxide number of from about 1 to about 5, and a specific gravity of around 0.7745.

The chlorination product employed in this example for further alkylation to yield an alkylate consisting essentially of di-alkylbenzene compounds contained 12 mole percent chloroparaffins, the majority of which were monochlorinated as hereinbefore described.

Into a 5 liter, creased, 3-necked flask were charged the chloroparaffin alkylating agent, the monoalkylbenzene produced by propylene tetramer alkylation as described above and ten grams of anhydrous aluminum chloride. The mixture was mechanically agitated and heat was applied to heat the reaction mass to between 60° and 65°C. The temperature was maintained in this range for a period of 1 hour, after which five additional grams of anhydrous aluminum chloride were added to the reaction mixture. After an additional one hour period, the reaction mass was decanted from the sludge into a separatory funnel and gravity settled. After settling overnight, 44 grams of acid sludge were isolated from the reaction mixture. The hydrocarbon layer was washed with water, aqueous sodium hydroxide solution and again with water until essentially neutral. There were isolated 2,031 grams of crude alkylate. The product was dried overnight over calcium sulfate and filtered. The alkylate was then distilled to recover 156.5 grams of bottoms alkylate boiling above 192°C at 5mm. Hg. The molecular weight of the bottoms alkylate was 445 and infrared analysis indicated the following approximate isomer distribution for the alkylbenzenes:

Isomer	Mole Percent
para dialkyl	71.1
meta dialkyl	13.8
monoalkyl	15.1

Seventy-five grams of alkylate bottoms produced as described above in this example were charged to a one liter, creased 3-necked flask along with 60.5 grams of 100 pale oil. 123.5 grams of 20 percent oleum was then charged to the flask and the reaction was allowed to attain a temperature of 50° to 55°C. This temperature was maintained during the remainder of the oleum addition. The reaction mass was then poststirred for 30 minutes at about 60°C., and then charged to a separatory funnel and gravity settled overnight at 45° to 50°C.

After removal of the primary acid sludge on the following day, the crude acid-oil remaining was diluted and mixed with 252 ml. of hexane. The mixture was then gravity settled at ambient temperature overnight and a secondary sludge split was taken, and the following data were recorded at this point for the crude acid-oil remaining after the secondary sludge split:

	Sulfonic Acid Solution	
	Total Acid, meq./g.	0.904
	Sulfonic Acid, meq./g.	0.549
	Combining Weight (RSO ₃ H)	421
5	Total Sludge Recovered, g.	120.4
	Wt. Ratio, Total Sludge/Oleum Charged	0.98
	Yield RSO ₃ H/alkylate by Weight	0.85
	Acid Ratio	7.6

The sulfonic acid was purified by calcium hydroxide treatment followed by nitrogen degassing. The purified acid was then converted to an overbased barium sulfonate composition employing methanolic barium oxide as hereinbefore described. The resulting overbased sulfonate was bright and fluid at ambient temperature. The purified sulfonic acid and the sulfonate produced therefrom had the following analyses:

	Purified Sulfonic Acid	
	Total Acid, meq./g.	0.540
	Sulfonic Acid, meq./g.	0.501
20	Wt. Percent Nonvolatiles	44.4
	Overbased Barium Sulfonate	
	Base Number (Acetic Acid Method)	72
	Weight Percent Barium Sulfonate	44.3

Oil blends to which the overbased barium sulfonate were added remained stable and bright after 90 days in storage at ambient temperature and at 50°C.

EXAMPLE 17

In this example, a biodegradable detergent alkylate prepared by the procedure described in Example 1, but using the alkylation reactant ratio and chlorination product described in Example 7 was subjected to further alkylation by reacting this alkylate with propylene tetramer prepared as described in Example 16.

The propylene tetramer was actually, as is understood in the art, a mixture of highly branched alkenes having the following composition in terms of carbon atom content as determined by mass spectrometer.

Alkene	Mole Percent
C ₉	0.81
C ₁₀	1.69
C ₁₁	29.04
C ₁₂	51.68
C ₁₃	13.84
C ₁₄	4.81
C ₁₅	2.34
C ₁₆	0.79

The boiling range of the tetramer was from 350°F to 416°F, its average molecular weight was 185 and its bromine number was 97.

The detergent alkylate subjected to further alkylation by reaction with the propylene tetramer mixture contained 90.2 weight percent of mono-n-alkylate, about 9.8 weight percent tetralins and a trace of naphthalenes as determined by mass spectrometer.

The object of this procedure was to determine the effect of adding a branched chain alkyl substituent to a monosubstituted alkylate in which the single alkyl substituent thereof was straight chain or linear.

Three hundred sixty-three grams of the detergent alkylate and 8.3 grams of anhydrous aluminum chloride catalyst were placed in a 2 liter, 3-necked flask with mechanical agitation. The reactants were then saturated with gaseous HCl and warmed to a temperature of 55°C, whereupon the propylene tetramer alkylating agent was charged to the flask over a period of 25 minutes by means of a dropping funnel and while holding the temperature at between 55° and 60°C. An addi-

tional 8.3 grams of the aluminum chloride catalyst was added to the reaction mixture after about half of the propylene tetramer was charged to the flask, and the reaction mixture was then again saturated with gaseous HCl. The reaction mass was poststirred for a period of about 1 hour at 55° to 60°C. A product layer was decanted from the sludge phase into a separatory funnel and worked-up essentially as described in Example 10.

From the reaction mass there were isolated 490.6 grams of crude alkylate. A portion of this alkylate was fractionated to a cut point of 193°C at 5 mm. Hg. to yield 191.6 grams of bottoms alkylate. The average molecular weight of the bottoms alkylate was 413 and infrared analysis indicated the following approximate isomer distribution for the alkylbenzenes therein:

Isomer	Mole Percent
para dialkyl	77.0
meta dialkyl	16.4
mono alkyl	6.7

The bottoms alkylate prepared as above described was sulfonated with 20 percent oleum at a sulfonation weight ratio of 1.5 to 1, oleum to alkylate. The sulfonic acid yielded from the sulfonation was purified as described in Example 10 and an overbased barium sulfonate was prepared. The analyses of the sulfonic acid and the barium sulfonate prepared therefrom were as follows:

Purified Sulfonic Acid	
Total Acid, meq./g.	0.483
Sulfonic Acid, meq./g.	0.461
Wt. Percent Nonvolatiles	42.9
Overbased Barium Sulfonate	
Base Number	72
Wt. Percent Sulfonate	44.4

Lubricating oil compatibility tests showed that lubricating oils to which the sulfonate composition was added remained bright after storage for 90 days at ambient temperatures, and developed only a trace of precipitate after storage at 50°C for this period of time.

SULFONATES FROM HYDROCARBON COMPOSITIONS BY DISPROPORTIONATION REACTION

Since filing the parent application (Ser. No. 529,284) it has been discovered that the product prepared by disproportionation of mono-n-alkaryl compounds in addition to dialkaryl compounds contains a minor, but significant, amount of alkyl-substituted tetrahydronaphthalenes having molecular weights similar to the dialkaryl compounds.

In utilizing a disproportionation reaction to prepare a hydrocarbon composition which can be converted to oil soluble sulfonates, a starting material is employed which consists essentially of mono-n-alkaryl compounds of a certain specific character. More specifically described, these mono-n-alkaryl compounds are characterized in having an aromatic nucleus which is mono-substituted by a straight chain or normal alkyl group containing from eight to 18 carbon atoms and attached to the aryl group through a secondary carbon atom. The aromatic compound or compounds from which the mono-n-alkaryl starting material is derived can be benzene, toluene or xylene or mixtures thereof, but is preferably benzene. It is preferable that the alkyl substituents of the compounds contain from 10 to 16 carbon atoms and most preferred that the alkyl substit-

uent not differ by more than four carbon atoms in chain length.

The mono-n-alkaryl starting material can be conveniently derived from petroleum, and a preferred source of the starting material is the detergent alkylate prepared from petroleum as described in U.S. Pat. No. 3,316,204. This alkylate is rich in mono-n-alkaryl compounds meeting the definition above, and can be used in this method of the present invention without further purification or treatment. Usually the detergent alkylate will contain at least 90 weight percent mono-n-alkaryl compounds of the type described. Also the mono-n-alkaryl compounds in the detergent alkylate are characterized in having at least 95 percent of the alkyl groups bonded to the aryl nucleus through a secondary carbon atom of the respective alkyl group.

In carrying out the disproportionation reaction used in this process, the mono-n-alkaryl starting material is initially heated to a temperature of from about 20°C to about 130°C. Maximum yields of the desired di-n-alkaryl product are obtained, however, at temperatures between about 74°C and 120°C. The most preferred temperature for use in the reaction is about 100°C. The reaction is most suitably carried out at atmospheric pressure, although sub- and superatmospheric pressures can also be employed. Either a batch or a continuous process can be used.

The catalyst used in the disproportion reaction is aluminum chloride, aluminum bromide or mixtures thereof. A suitable amount of catalyst is from about 0.1 to about 10 weight percent, based on the mono-n-alkaryl starting material. Preferably, the amount of catalyst is from about 0.5 to about 3 weight percent on the same basis. The most preferred operating conditions require the use of about 0.5 weight percent of the catalyst and a temperature of about 100°C. A small amount of water or HCl is added to the reaction with the catalyst and functions as a catalyst employed. The reaction time for the disproportionation reaction is at least 5 minutes and preferably from about 30 minutes to 3 hours.

When the described preferred conditions and preferred amounts of material are utilized, from about 30 to about 60 mole percent of the mono-n-alkaryl starting material is converted to products. The products include di-n-alkaryl compounds, alkyl-substituted tetrahydronaphthalenes of similar molecular weight, relatively low molecular weight aromatic compounds, and relatively low molecular weight straight chain alkane compound. There are also small amounts of undesirable higher molecular weight materials, such as naphthalenes, trialkaryl compounds and diphenylalkanes. These higher molecular weight materials are difficult to separate from the di-n-alkaryl product. However, we have found that the quantity of these undesirable high molecular weight products can be minimized by controlling the reaction conditions and, particularly, the temperature, amount of catalyst and reaction time, so as to limit the amount of mono-n-alkaryl starting material which is converted to product to from about 30 to about 50 mole percent. At this extent of conversion, selectivity to the desired di-n-alkaryl product is maximum and is from about 75 percent to 95 percent.

After cessation of the process, the unreacted mono-n-alkaryl compounds, low molecular weight aromatic compounds, the low molecular weight alkane compounds and most of the diphenylalkane compounds are

separated by fractional distillation from the desired di-n-alkaryl compounds and the small amount of high molecular weight heavy bottoms material. The desired separation can be effected by distilling to a cut point of about 200°C at 10 mm. Hg. to remove all of the materials boiling therebelow.

The disproportionation reaction can be carried out by either a continuous or a batch process.

The bottoms material remaining after the described final fractionation of the disproportionation product is an alkylate containing a minor amount of diphenylalkanes, from about 8 to 25 weight percent alkyl-substituted tetrahydronaphthalenes and from about 64 to 85 weight percent di-n-alkaryl compounds in which the alkyl substituents contain from eight to 18 carbon atoms and are, to the extent of at least 95 percent, bonded to the aryl portion of the compounds through a secondary carbon atom. It is preferred that substantially all of the alkyl substituents of the di-n-alkaryl compounds do not differ from each other in chain length by more than four carbon atoms.

The alkylate hydrocarbon composition consisting essentially of di-n-alkaryl compounds yielded by the disproportionation reaction are further treated to convert them to the novel oil soluble metal sulfonate compositions of the present invention. In general, this is achieved by the use of conventional sulfonation, neutralization and overbasing procedures now well understood in the art. For a complete understanding of these procedures, reference is again made to U.S. Pat. No. 3,316,294 relative to sulfonation, and to U.S. Pats. Nos. 2,861,951 to Carlyle; 3,150,088 to Hunt et al; and 3,150,089 to Hunt relative to various types of neutralization and over-basing procedures. In general, the oil soluble di-n-alkaryl sulfonic acids produced on sulfonation are reacted with metal inorganic base compounds, metal alcoholates, or metal lower alkoxyethanolates to yield a neutral oil soluble metal sulfonate composition, or an oil soluble metal sulfonate composition having reserve alkalinity by reason of the dispersion therein of an excess amount of metal hydroxide or carbonate particles derived from one of the described metal neutralizing agents. The metal compounds used are preferably compounds of barium, magnesium or calcium.

The sulfonate compositions which are prepared from the alkylates yielded by the disproportionation reaction possess improved properties even with respect to those sulfonates which are derived from the bottoms alkylate yielded in the detergent alkylate process hereinbefore described. The superiority of the sulfonates derived via disproportionation is believed to be due to the higher percentage of di-n-alkaryl compounds in the alkylate. The alkyl-substituted tetrahydronaphthalenes in the alkylate appear to sulfonate about as readily as the di-n-alkaryl compounds and have a neutral effect on the properties of the sulfonated composition. Particularly noteworthy is the low viscosity of the neutral and overbased sulfonates derived from the disproportionation product since this property permits these sulfonates to be blended with conventional sulfonate compositions which are prepared by other well known procedures but lack sufficient fluidity to be used in many applications.

A relationship is known to exist between the activity (weight percent of pure metal sulfonate salt), the base number (degree of reserve alkalinity or overbasing) and the viscosity of overbased metal sulfonate compo-

sitions of the general type under consideration. This relationship is such that increasing the base number or activity of the compositions generally results in an increase in viscosity until the compositions become too viscous at ordinary temperature to facilitate practical usage. This relationship is graphically illustrated and is described in Hunt et al U.S. Pat. No. 3,150,088.

The oil soluble metal sulfonate compositions as prepared from the di-n-alkaryl compound-rich disproportionation reaction bottoms are unusual in the extent of overbasing and concurrent high activities which can be attained in these compositions without an intolerable loss in fluidity. Thus, for example, calcium di-n-alkylbenzene compositions can be prepared which are characterized in having an acetic acid base number exceeding 400, an activity exceeding 20 percent, and a viscosity of less than 350 centistokes at 210°F (sufficiently fluid to permit use in nearly all applications). Magnesium di-n-alkylbenzene compositions having a base number exceeding 375, an activity exceeding 25 percent and a viscosity of less than 100 centistokes at 210°F have been prepared. A barium di-n-alkylbenzene composition having a base number of 195, an activity of 45 percent and a viscosity of 692.6 centistokes at 210°F has been prepared.

The following examples will serve to illustrate the preparation of oil soluble metal sulfonates which possess the desirable properties hereinbefore described and the disproportionation reaction.

EXAMPLE 18

This example will serve to illustrate the preparation of a di-n-alkylbenzene alkylate from a detergent alkylate produced in Example 3 using the disproportionation procedure. This detergent alkylate was determined by mass spectrometer analysis to have the following composition:

Component	Weight Percent
Mono-n-alkylbenzene	92.8
Diphenylalkane	—
Tetrahydronaphthalenes	7.1
Naphthalenes	0.1
Average Molecular Weight	261

The detergent alkylate was further analyzed by mass spectrometer and gas liquid partition chromatography for isomeric content as follows:

Alkyl Chain Length	Weight Percent Mass. Spec.	GLPC
C ₁₀	—	0.1
C ₁₁	1.60	1.6
C ₁₂	17.2	15.2
C ₁₃	54.6	51.4
C ₁₄	26.4	26.9
C ₁₅	0.2	4.6

Number of Alkyl Group Carbon Atom Attached to Benzene	Weight Percent
1 (Primary)	0.5
2 (Secondary)	24.4
3 do.	15.9
4 do.	16.3
5 do.	17.9
6 do.	17.1
7 do.	8.0

The detergent alkylate as thus produced was continuously pumped into a two stage disproportionation reactor unit. One weight percent of AlCl₃ catalyst based on the weight of the detergent alkylate was continuously added to the first reactor stage with a trace of HCl. The

reacting material was then permitted to move into the second reactor stage after addition of the catalyst. The residence time in the two stage reactor was 3 hours. Both stages of the reactor were held at 75°C.

A sample of the product developed in the second reactor was collected and the sludge removed therefrom. Analysis of the sludge-free sample indicated that disproportionation of the detergent alkylate under these conditions resulted in a conversion of 33.5 mole percent of the detergent alkylate starting material. On the basis of the total alkylate consumed in the reaction, the weight percent yields of the various products with the exception of a very small amount of high molecular weight product were as follows:

Di-n-alkylbenzene*	67.3
n-paraffins	12.7
Sludge	5.7
Benzene	13.7

* A minor amount of alkyl-substituted tetrahydronaphthalenes was present in this fraction.

EXAMPLE 19

The di-n-alkylbenzene product of the disproportionation reaction described in Example 18 was isolated by fractionation and was then subjected to sulfonation by initially placing 1,500 grams of the di-n-alkylbenzene and 1,210 grams of 100 pale oil in a reaction flask. This mixture was contacted with 2,250 grams of 20 percent oleum under sulfonation conditions. A yield of 1.2 pound of oil soluble sulfonic acid per pound of the di-n-alkylbenzene disproportionation reaction product was obtained from the sulfonation reaction.

EXAMPLE 20

Three thousand grams of the detergent alkylate described in Example 18 was contacted at 100°C and for a period of two hours with 15 grams of aluminum chloride activated by a trace of HCl. 47 mole percent of the detergent alkylate was converted to products and the yield of di-n-alkylbenzene was 0.7 pound per pound of the alkylate consumed.

EXAMPLE 21

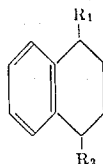
One thousand grams of the detergent alkylate described in Example 18 was contacted at 100°C for a period of 2.5 hours with 5 grams of aluminum chloride activated by a trace of HCl. 47.3 mole percent of the detergent alkylate was converted to products and 0.71 pound of di-n-alkylbenzene was produced for each pound of the alkylate consumed.

EXAMPLE 22

This example illustrates that the hydrocarbon composition produced by the herein described disproportionation reaction contains a minor but substantial amount of alkyl-substituted tetrahydronaphthalenes.

The monoalkylate composition used as the starting material was produced by the process of U.S. Pat. No. 3,316,294 and had the following analysis:

	Mole or Weight
monoalkylbenzenes*	89.5%
tetrahydronaphthalenes**	10.5%
* C ₁₁ -C ₁₄ alkyl groups, with a predominance of C ₁₃	
** Represented by the formula:	



wherein R₁ and R₂ contain from one to 13 carbon atoms each, with the sum of R₁ and R₂ being from about 4 to about 14.

An amount of 1,500 grams of the monoalkylate composition was charged to an autoclave. To this were added 20 grams AlCl₃ (1.3 percent by weight based on monoalkylate) and 0.3 gram water. The contents of the autoclave were stirred for 2 hours while maintaining the temperature at 110°C. The reaction mixture was then settled and the catalyst withdrawn. The reaction product was washed with an aqueous base. Following this the reaction product was fractionally distilled using a cut-point of 197°C. at 10mm Hg. The product (bottoms fraction) had a yellow to brown color. It contained 67.1 percent dialkylbenzenes* and 24.4 percent alkyl-substituted tetrahydronaphthalenes, with the remaining 8.5 percent a mixture of naphthalenes, dihydronaphthalenes, and diphenylalkanes. The product had the following physical properties:

Pour Point, °F.	-65
Viscosity at -40°F.	12,066
Viscosity at 100°F.	32.84
Viscosity at 210°F.	5.41
Viscosity Index	110

* The percent conversion of monoalkylbenzenes to dialkylbenzenes was 45%.

EXAMPLE 23

This example illustrates the preparation of oil soluble neutral and overbased metal sulfonate compositions using the disproportionation process and further illustrates the improved viscosity property of these sulfonates.

Two detergent alkylbenzene alkylates were prepared using the general procedure referred to in Example 3 except that partially monochlorinated C₁₂-C₁₄ n-paraffins were employed in reactant mole ratios of 9:1 and 8:1 benzene to chloroparaffins, respectively, in the two samples. These alkylates were then each subjected to disproportionation, followed by removal of paraffins and unsubstituted benzene from the disproportionation reaction product by fractional distillation. Following the fractionation, the two dialkylbenzene-containing fractions remaining had the following weight percent analyses by mass spectrometer.

Disproportionated Alkylate Sample	A	D
Di-n-alkylbenzenes*	97.3	95.4
Diphenylalkanes	1.9	2.3
Naphthalenes	1.7	2.3
Molecular Weight	455	450

* A minor amount of alkyl-substituted tetrahydronaphthalenes was present in this fraction.

Purified sulfonic acids were prepared from these alkylates by treatment with oleum containing 20 weight percent SO₃. The sulfonations were carried out in 100 pale oil at a weight ratio of 1.5:1, oleum to disproportionated alkylate. After the primary sludge split, the crude acid-oils were diluted with n-hexane and a secondary sludge split was taken after gravity settling. The crude sulfonic acids were purified by treating with calcium hydroxide and blowing with nitrogen. The purified sulfonic acids were then used to prepare oil soluble barium sulfonate compositions.

Sample B was simultaneously neutralized and overbased with methanolic barium oxide in accordance with the procedure described in Carlyle U.S. Pat. No. 2,861,951. Sample A was merely neutralized using methanolic barium oxide. For the purpose of comparing these sulfonates with the types of oil soluble sulfonates heretofore in used and made by previously utilized procedures, several tests and analyses of these sulfonates and an oil soluble barium sulfonate derived from postdodecylbenzene (previously described in Example 12) were carried out. The postdodecylbenzene sulfonate here under comparison was prepared by the same neutralization and overbasing procedure used to prepare the barium sulfonates from the disproportionation reaction alkylate. The results of these comparative tests were set forth in Table VIII.

TABLE VIII

Barium Sulfonate Sample Base Number *	A (neutral)	B	From Postdodecylbenzene Alkylate
Wt. Percent Barium Sulfonate	4.1	70	72
Viscosity, centistokes at 210°F	53.7	46.7	44.6
	20.01	25.03	64.3

* Base number was determined by acetic acid method described in Analytical Chemistry, Vol. 23, No. 2, February, 1951, and Vol. 24, No. 3, March, 1959, P. 519.

In referring to the data set forth in Table VIII, it will be noted that the sulfonate compositions prepared from disproportionated detergent alkylate possessed much lower viscosities than the conventional sulfonate prepared from postdodecylbenzene alkylate. The low viscosity of the neutral alkylate was particularly striking since it has previously been impractical to prepare neutral barium sulfonate compositions of this activity (percent barium sulfonate) from such widely used starting materials as postdodecylbenzene or mahogany sulfonic acids due to the very viscous nature of such sulfonate compositions.

EXAMPLE 24

The neutral barium sulfonate derived from Sample A in Example 24 was added to a turbine oil base stock having an overall viscosity of 160 S.S.U. at 100°C. Certain other conventional additives were also added to the turbine oil base stock in small amounts.

Similar compositions using the same turbine oil base stock and conventional additives, but using a barium sulfonate derived from postdodecylbenzene alkylate were made up for comparison purposes.

Both treated turbine oils were then subjected to rust inhibition and water demulsibility tests in accordance with ASTM D-665 and D-1401, respectively. The results of these tests were set forth in Table IX.

TABLE IX

Turbine Oil Blend Additives	1	2
Anti-oxidants	0.45	0.45
Neutral Sulfonate from Sample A, Example 19	0.10	
Postdodecylbenzene alkylate sulfonate		0.12
Test Results		
Rust Test*	Pass	Fail
Water Emulsion**	40-40-0-20	29-0-51-60

* ASTM D-665

** ASTM D-1401 conducted at 130°F. The four values reported are, in order, ml. in oil layer, ml. in water layer, ml. in cuff or emulsion, and time of standing in minutes.

EXAMPLE 25

Twenty-seven thousand four hundred nine grams of detergent alkylate prepared as described in Example 3 and containing about 90 weight percent mono-n-alkylbenzene compounds were contacted at a temperature of 75°C for 1.5 hours with 206 grams of aluminum chloride containing a trace amount of HCl. 1,168 grams of sludge were separated from the reaction mixture. 50.5 mole percent of the mono-n-alkylbenzene compounds were converted to product in the disproportionation reaction. Unreacted detergent alkylate, benzene and paraffins were separated from the disproportionation reaction mixture by distilling to a cut point of 205°C at 20 mm. of Hg. to yield 8,899 grams of bottoms alkylate rich in di-n-alkylbenzene compounds.

A portion of bottoms alkylate was then subjected to sulfonation in the manner hereinbefore described to produce a sulfonic acid composition containing 51.6 weight percent n-hexane, 20 weight percent 100 pale oil and 28.4 weight percent di-n-alkylbenzene sulfonic acid having an average molecular weight of 490. 100 grams of this sulfonic acid composition were placed in a 1 liter, 3-necked flask with 23.6 grams of 80 pale oil and 1.8 grams of a mixture consisting of 70 volume percent of water and 30 volume percent of 2-methoxyethanol. The flask was equipped with a mechanical stirrer, two dropping funnels, a thermometer and a condenser.

The mixture in the flask was heated to about 35°C and the acid was neutralized with 16 grams of a calcium 2-methoxyethanol carbonate complex solution containing 7.4 weight percent of calcium and prepared by the method described in Hunt et al. U.S. Pat. No. 3,150,088. After the neutralization, the temperature was adjusted to 40°C and the following were added simultaneously at a constant rate:

Three hundred eighteen grams of the calcium 2-methoxyethanol carbonate complex solution over a period of 1 hour.

25.4 grams of a mixture consisting of 70 percent by volume water and 30 volume percent 2-methoxyethanol over a period of 48 minutes.

After the additions, the volatile solvents were removed by heating the mixture to 150°C and then stripping with CO₂ gas for about 20 minutes. The product overbased calcium sulfonate composition had an acetic base number of 454 (this is equivalent to 40.5% CaCO₃) and contained 22.5 weight percent calcium di-n-alkylbenzene sulfonates. About 37 weight percent nonvolatile oil soluble hydrocarbons were present in the composition and it had a viscosity of 314.2 centistokes at 210°F.

EXAMPLE 26

A 1 liter, 3-necked flask equipped as described in Example 8 was charged with 200 grams of the sulfonic acid prepared as in Example 8 along with 37.6 grams of 80 pale oil and 2.0 grams of a mixture consisting of 70 volume percent water and 30 volume percent 2-methoxyethanol. The mixture was heated to about 40°C and the sulfonic acid was neutralized with 20 grams of a magnesium 2-methoxy-ethanol carbonate complex solution prepared by the method described in Hunt U.S. Pat. No. 3,150,089. The solution of the complex contained 7.9 weight percent magnesium.

After the neutralization, the temperature was adjusted to 45°C and the following were added simultaneously at constant rates:

Two hundred thirty-three grams of the magnesium complex solution over a period of 150 minutes.

Sixty grams of the water-2-methoxyethanol mixture over a period of 150 minutes.

Sixty grams of the water-2-methoxyethanol mixture over a period of 135 minutes.

After the additions, the volatile solvents were removed by heating to 150°C and then stripping the CO₂ gas for about 20 minutes. The product sulfonate composition was bright, clear and fluid. It had an acetic base number of 389 (this is equivalent to 28% MgCO₃), contained 30 weight percent magnesium di-n-alkylbenzene sulfonate and had a viscosity of 96 centistokes at 210°F. About 28 weight percent nonvolatile oil soluble hydrocarbon compounds were present in the composition.

While it is believed to be inherent from the foregoing description and from general usage in the prior art, the term "nonvolatile oil soluble hydrocarbon compounds" as used herein refers to both the unsulfonated feedstock and to intentionally added materials. In some cases, these intentionally added materials are added during the sulfonation of the feedstock and are therefore concurrently present in the final sulfonate product.

Examples of suitable nonvolatile oil soluble hydrocarbons, other than the unsulfonated hydrocarbons, include mineral lubricating oils obtained by any of the conventional refining procedures. Examples of suitable mineral lubricating oils include the pale oils and the bright stocks. In addition to the nonvolatile oil soluble hydrocarbon compounds, in some instances the intentionally added material can be liquid synthetic lubricating oils, such as polymers of propylene, polyoxyalkylenes, polyoxypropylene, dicarboxylic acid esters, such as esters of adipic and azelaic acids with alcohols such as butyl, 2-ethylhexyl and dodecyl alcohols.

While particular embodiments of the invention have been described, it will be understood that the invention is not limited thereto, since many modifications may be made; and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention. For example, though the foregoing examples have described the preparation of calcium, magnesium and barium sulfonates produced in accordance with several neutralizing and over-basing procedures hereinbefore known to the art, which are intended to comprehend and encompass other neutral and overbased sulfonates of other base metals. Such metals include, for example, zinc, tin, cobalt, manganese, titanium, lead, copper, cadmium, the alkali metals, the alkaline earth metals, and ammonium ions. The novel sulfonate products also are intended to include ethylene diamine and other oil soluble amine sulfonates.

We claim:

1. An oil soluble metal di-n-alkaryl sulfonate composition having a viscosity in centistokes at 210°F of less than 750, and comprising:

A. From about 20 to about 80 percent by weight metal di-n-alkaryl sulfonate compounds in which the alkyl substituents contain from eight to 18 carbon atoms and are, to the extent of at least 95 percent, bonded to the aryl nucleus through a second-

ary carbon atom, the aryl moiety of said di-n-alkaryl being selected from the group consisting of phenyl, tolyl, xylyl, naphthyl and mixtures thereof; and

B. Correspondingly from about 80 to about 20 percent by weight nonvolatile oil soluble hydrocarbon compounds selected from the group consisting of unsulfonated feedstock, mineral lubricating oils and mixtures thereof.

2. The oil soluble metal di-n-alkaryl sulfonate composition of claim 1 wherein the metal is an alkali or alkaline earth metal.

3. The oil soluble metal di-n-alkaryl sulfonate composition of claim 2 wherein the metal is magnesium, calcium, barium or mixtures thereof.

4. The oil soluble metal di-n-alkaryl sulfonate composition as described in claim 1 characterized further in that it contains at least 35 weight percent metal di-n-alkaryl sulfonate compounds.

5. The oil soluble metal di-n-alkaryl sulfonate composition as described in claim 2 characterized further in that it contains at least 50 weight percent metal di-n-alkaryl sulfonate compounds.

6. The oil soluble metal di-n-alkaryl sulfonate composition of claim 5 wherein the metal is an alkali or alkaline earth metal.

7. The oil soluble metal di-n-alkaryl sulfonate composition of claim 6 wherein the metal is magnesium, calcium, barium or mixtures thereof.

8. An oil soluble metal dialkaryl sulfonate composition comprising oil soluble metal dialkaryl sulfonates in which one of the alkyl substituents is a C₉-C₁₆ branched chain alkyl group and the other alkyl substituent is a C₈-C₁₈ straight chain alkyl group and wherein the aryl moiety is selected from the group consisting of phenyl, tolyl, xylyl, naphthyl and mixtures thereof.

9. The oil soluble metal dialkaryl sulfonate composition of claim 8 wherein the branched chain alkyl group is a substantially C₁₂ alkyl group.

10. The oil soluble metal dialkaryl sulfonate composition of claim 9 wherein the straight chain alkyl group contains from about 10 to about 16 carbon atoms.

11. The oil soluble metal dialkaryl sulfonate composition of claim 8 wherein the difference in the number of carbon atoms of the branched chain alkyl group and the straight chain alkyl group does not exceed 4.

12. An oil soluble metal sulfonate composition comprising:

A. From about 64 to about 85 weight percent metal di-n-alkaryl sulfonate compounds the alkyl groups of which each contain from about eight to about 18 carbon atoms and the aryl moiety is phenyl, tolyl, xylyl, or mixtures thereof, and

B. from about eight to about 25 weight percent metal alkyl-substituted tetrahydronaphthalene sulfonate compounds.

13. The oil soluble metal sulfonate compositions of claim 12 wherein the aryl moiety of said di-n-alkaryl sulfonate compounds is phenyl.

14. The oil soluble metal sulfonate composition of claim 13 wherein the molecular weight of the alkyl-substituted tetrahydronaphthalene sulfonate is substantially in the same range as the molecular weight of the metal di-n-alkaryl sulfonate compounds.

15. The oil soluble metal sulfonate composition of claim 14 wherein the metal is an alkali or alkaline earth metal.

16. The oil soluble metal sulfonate composition of claim 15 wherein the metal is magnesium, calcium, barium or mixtures thereof.

17. An oil soluble calcium hyperbasic sulfonate composition comprising:

- A. over 20 weight percent calcium di-n-alkylbenzene sulfonate compounds in which the alkyl substituents contain from 10 to 16 carbon atoms;
- B. basic calcium compounds in an amount imparting to said composition an acetic base number exceeding 400; and
- C. the balance of the composition consisting essentially of nonvolatile oil soluble hydrocarbon compounds selected from the group consisting of unsulfonated feedstock, mineral lubricating oils and mixtures thereof;
- D. said composition having a viscosity in centistokes of less than 350° at 210°F.

18. The oil soluble hyperbasic calcium sulfonate composition as described in claim 17 wherein said basic calcium compounds are present in an amount imparting to said composition an acetic base number exceeding 450 and said composition has a viscosity in centistokes of less than 325° at 210°F.

19. An oil soluble hyperbasic magnesium sulfonate composition comprising:

- A. over 25 weight percent magnesium di-n-alkylbenzene sulfonate compounds in which the alkyl substituents contain from 10 to 16 carbon atoms;
- B. basic magnesium compounds in an amount imparting to said composition an acetic base number exceeding 375; and
- C. the balance of the composition consisting essentially of nonvolatile oil soluble hydrocarbon compounds selected from the group consisting of unsulfonated feedstock, mineral lubricating oils and mixtures thereof.

20. The oil soluble metal di-n-alkaryl sulfonate composition of claim 3 wherein the aryl moiety is phenyl.

21. The oil soluble metal di-n-alkaryl sulfonate composition of claim 4 wherein the aryl moiety is phenyl.

22. The oil soluble metal di-n-alkaryl sulfonate composition of claim 7 wherein the aryl moiety is phenyl.

23. The oil soluble metal di-n-alkaryl sulfonate composition of claim 11 wherein the aryl moiety is phenyl.

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