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OIL-SOLUBLE SURFACE-ACTIVE AGENTS AND COMPOSITIONS CONTAINING THEM

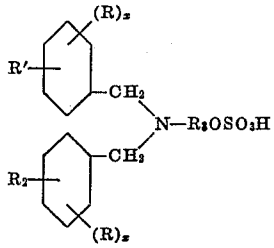
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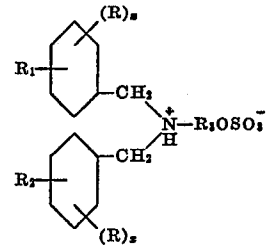
This invention relates to new and useful oil-soluble surface-active agents containing both anionic and cationic surface-active groups within the same molecule. More particularly, the invention relates to oil-soluble amino sulfates and compositions containing them.

The novel oil-soluble surface-active agents of this invention may be illustrated by reference to the following structural formula:



In the above formula R_1 and R_2 are the same or different alkyl groups of from 9 to 18 carbon atoms, R is a hydrogen or methyl group, x is an integer of from 1 to 3, and R_3 is an alkylene group of from 1 to 7 carbon atoms.

The above N,N,di-(alkylbenzyl)-amino alkyl sulfuric acids are ampholytic in nature and are capable of acting either as an acid or a base. In slightly acid solutions having pH's in the range of about 3 to 5 the molecule of these surface-active compounds forms within itself a zwitterion between the nitrogen group and the alkyl sulfate group. Under such conditions the zwitterion characteristics of the compounds may be conveniently illustrated by the following rearrangement of the above formula:



The surface-active agents of this invention in addition to their unusual ampholytic surface-active nature as described above are oil-soluble to a high degree. They possess excellent dispersing properties in lubricating and fuel oil compositions. Sludge-forming materials normally present in such compositions and particularly in fuel oils containing substantial amounts of cracked stock may be maintained in suspension for an indefinite period by these surface-active agents. Undesirable deposition of sludge and the resultant clogging of screens, filters and lines in lubricating and fuel oil systems are thus avoided.

The oil-soluble surface-active amino sulfates, according to this invention, are also excellent rust inhibitors. Hydrocarbon oil compositions often become contaminated with water and cause considerable rusting and corrosion of ferrous metal surfaces with which they come in contact. The surface-active compounds of this invention, when added to such hydrocarbon oil compositions, are remarkably effective in the prevention of corrosion and rust under similar conditions.

Another desirable feature of the surface-active agents of this invention is that they may be prepared directly from the proper alkanol amines by sulfation. The alkanol groups of the amines may be branched or straight-chain in nature and contain from 1 to 7 carbon atoms. Ethanol, n-propanol, iso-propanol and butanol types of amines are preferred for their availability and the unusual effectiveness of the compounds derived from them.

In accordance with the invention suitable di-(alkylbenzyl)-alkanol amines may be reacted with a sulfating agent such as sulfuric acid, fuming sulfuric acid or chlorsulfonic acid to produce this new and useful class of oil-soluble surface-active tertiary amino sulfates. The sulfation is generally carried out at temperatures of from 0° to 100° C., and preferably from 0° to 30° C. If desired for convenience in handling, solvents such as chloroform, methylene chloride, carbon tetrachloride, and the like, may be employed. Usually only a short time, from about 5 minutes to 2 hours, is required to complete the sulfation. Following the sulfation the product may be washed and neutralized to produce the oil-soluble surface-active tertiary amino sulfates.

Di-(alkylbenzyl)-alkanol amines which are particularly suitable for sulfation to the extraordinarily effective surface-active tertiary amino sulfates of this invention may be obtained by the reaction of alkylbenzyl chlorides with an alkanol amine. In the reaction about 2 molar proportions of alkylbenzyl chloride to 1 molar proportion of the alkanol amine are employed. The reaction is carried out in the presence of a mild neutralizing agent, preferably sodium bicarbonate, while warming slightly, usually in the temperature range of from 50° to 100° C. The chemical structure of the di-(alkylbenzyl)-alkanol amines which contributes greatly to the unusually effective surface-active properties of the oil-soluble tertiary amino sulfates of this invention is determined by the type of alkylbenzyl chloride employed. Suitable alkylbenzyl chlorides may be obtained by chloromethylation of alkyl benzene hydrocarbons of various types. The alkyl benzene hydrocarbons must have one long-chain alkyl group containing from 9 to 18 carbon atoms. From 1 to 3 methyl substituents on the benzene nucleus may also be present. Such alkyl benzene hydrocarbons are conveniently prepared by the alkylation of benzene, toluene, xylene or mesitylene with a suitable alkylating agent containing from 9 to 18 carbon atoms in the presence of a catalyst such as hydrogen fluoride. A preferred group of alkylating agents for present purposes are the propylene polymers having from 9 to 18 carbon atoms. The unusual chemical stability of the propylene polymers toward alkylating catalysts and sulfating agents, derived apparently from their characteristically moderate chain-branching, renders them particularly suitable. Benzene and toluene are the preferred aromatic hydrocarbons in view of their availability and the high degree of effectiveness characteristic of the compounds containing them.

The novel oil-soluble surface-active tertiary amino sulfates of this invention and the process of preparing them are illustrated further by the following specific examples.

EXAMPLE 1

Preparation of N,N,di-(dodecylbenzyl)-ethanolamine

140 parts of dodecylbenzyl chloride obtained by chloromethylation of a propylene tetramer substituted benzene was added dropwise to a mixture of 16 parts of ethanolamine and 42 parts of sodium bicarbonate in an isopropanol-water solution. The addition was carried out over a period of one hour at a temperature of from 49° to 52° C. with stirring. The stirred mixture was then refluxed for two hours, filtered to remove inorganic salts and diluted with mixed hexanes. The solution was washed with water, dried over anhydrous calcium sulfate and concentrated under reduced pressure to give 145 parts of N,N,di-(dodecylbenzyl)-ethanolamine in the form of a yellow oil.

EXAMPLE 2

Preparation of 2-[N,N,di-(dodecylbenzyl)-amino]-ethyl sulfuric acid

21 parts of N,N,-di-(dodecylbenzyl)-ethanolamine prepared according to the method of Example 1 above was dissolved in 50 parts of chloroform and added portionwise to a solution of 13 parts of chlorosulfonic acid in 25 parts of chloroform. The addition was carried out at a temperature of from 20° to 30° C. After the addition was complete the reddish brown reaction mixture was stirred at 30° to 35° C. for 2 hours and then poured onto 50 parts of ice. The resultant water layer was removed and discarded and the chloroform layer was washed with water, neutralized to a pH of about 4.0 with silute sodium hydroxide solution and then concentrated under reduced pressure to give 18 parts of 2-[N,N,di-(dodecylbenzyl)-amino]-ethyl sulfuric acid in the form of a reddish brown glassy semi-solid. This crude product was tested without purification and was found to have excellent surface-active properties.

EXAMPLE 3

Preparation of 2-[N,N,di-(nonylbenzyl)-amino]-ethyl sulfuric acid

50 parts of N,N,di-(nonylbenzyl)-ethanolamine prepared from propylene trimer substituted benzyl chloride in accordance with the method of Example 1 was dissolved in 75 parts of chloroform and added dropwise to a solution of 17.5 parts of chlorosulfonic acid in 50 parts of chloroform. The addition was carried out at a temperature of from 6° to 8° C. Following the addition the mixture was stirred at 60° C. for 15 minutes and poured onto 150 parts of ice. The chloroform solution was washed twice with water and concentrated under reduced pressure to give crude 2-[N,N,di-(nonylbenzyl)-amino]-ethyl sulfuric acid in the form of a yellow viscous semi-solid. This crude product was dissolved in 200 parts of 90% methanol and extracted twice with 100-part portions of mixed hexanes. The methanolic solution was then concentrated to about one-half the original volume, cooled and filtered. The residue consisting of substantially pure 2-[N,N,di-(nonylbenzyl)-amino]-ethyl sulfuric acid was dried under reduced pressure at 70° C. to 32 parts of a yellow semi-solid. This material on analysis for nitrogen and sulfur gave the following results:

	Calculated from Theoretical	Found by Analysis
Percent Nitrogen	2.44	2.49
Percent Sulfur	5.59	5.27

In the above examples the proportions given are on a weight basis unless otherwise specified.

The present invention as mentioned above is also concerned with the preparation of improved hydrocarbon fuels, more particularly hydrocarbon fuels having improved properties as burner fuels, diesel engine fuels and jet fuels.

In the production of hydrocarbon fuels of the above type it is desirable economically to employ considerable quantities of cracked refinery stocks. Such stocks are becoming more and more available due to the ever-increasing use of thermal and catalytic cracking processes in petroleum refinery operations. These stocks when employed in burner fuels, diesel engine fuels and jet fuels, have the disadvantage of forming particles of sludge or gum which tend to deposit and cause plugging of filters, screens and lines. The necessity for frequent interruptions of burner and diesel and jet engine service to replace or unplug clogged filters and screens constitutes a serious problem.

Burner, diesel engine and jet fuel systems ordinarily contain certain amounts of water due to vapor condensation. The presence of this water tends to accelerate the formation of filter plugging gums and sludge in hydrocarbon fuels containing cracked stocks and also causes rusting of exposed ferrous metal surfaces, which rust in turn eventually loosens and causes clogging of filters and lines in the fuel oil system.

As a part of the present invention it has been discovered that by the addition of a small amount of the N,N,di-(alkylbenzyl) amino alkyl sulfuric acids described above to normally liquid hydrocarbon fuel, any tendency of the fuel to form filter-clogging particles of sludge or gum is substantially overcome. Such hydrocarbon fuel compositions in addition have the effect of inhibiting rusting of ferrous metal surfaces with which they come in contact, thus substantially eliminating rust particles that may also lead to clogging of fuel oil systems.

The hydrocarbon fuel base stocks suitable for use in the improved fuel oil compositions of this invention may be described broadly as petroleum distillates boiling in the range from about 175° C. to about 400° C. Such distillates are ordinarily characterized by an API gravity of at least 20° and usually at least 25°. The base stock may be either straight-run distillates or cracked distillates. The present invention finds its greatest utility in hydrocarbon fuels of the preceding types which contain substantial amounts of cracked distillates. Without the additives of this invention such fuels form appreciable amounts of filter-plugging sludge and gum which render them unsuitable for use in operations where uninterrupted service is desired, as is the case with most present-day operations.

Very small amounts of the N,N,di-(alkylbenzyl)-amino alkyl sulfuric acids in the order of 1% by weight or less have been found to be entirely effective to prevent line and filter clogging and to inhibit rusting when water is present in the system. Amounts in the range of from 0.001 to 0.20% by weight of the total fuel are particularly suitable and proportions in the range of from 0.005 to 0.015% by weight are most preferred in the more specific embodiments of the invention.

In order to facilitate evaluation of the improved fuel oil compositions of the present invention and avoid an enormous outlay of time and material, a rapid test method for determining filter-plugging characteristics was developed. The results of this test method have been found to correlate well with actual field tests using regular fuel oil burners and diesel and jet engines. The test is carried out by mixing 500 ml. of a fuel composition containing 0.01% by weight of additive with 500 ml. of water containing 102 parts per million hardness calculated as calcium magnesium carbonate, two thirds being calcium carbonate. The fuel oil composition and water are shaken in a separatory funnel for 30 seconds at the end of which they are allowed to stand for 10 minutes. At this point a phase separation occurs and an upper oil layer and a lower water layer are obtained, usually separated by an opaque cuff at their interface. This interface cuff is then filtered through a fritted glass crucible with the aid of a reduced pressure. Only as much water and oil are filtered as are necessary to assure complete extraction of the cuff, usually about 25 ml. However, in cases of severe emulsions the entire contents of the separatory funnel may have to be filtered. The resultant discoloration of the crucible mat by the particles of gum and sludge deposited is used as a comparative measure of the hydrocarbon fuel's tendency to plug filters and screens.

In the comparison the filter is compared with a standard series of 11 filters prepared in a similar manner from fuels of known filter-plugging tendencies. Standard filters are numbered zero to 10, the higher numbers being identified with the heavier deposits. For convenience, the rating given a particular test sample is termed its Interface Filter Deposit Rating (IFD) and denotes the number of the filter in the standard series with which it compares in amounts of filter deposits.

Table I, which follows, shows the IFD values of a number of fuel oil compositions according to the present invention as compared with a standard diesel, jet or burner fuel. The base fuel employed in each case was a mixture of equal parts of straight-run distillate from a waxy base crude, boiling in the range of from 196° C. to 357° C. and a Thermofor catalytic cracked fraction boiling in the range of from 192° C. to 297° C.

Table I

INTERFACE FILTER DEPOSIT RATING

Run No.	Additive	IFD No.
1	2-[N,N,di-(dodecylbenzyl)-amino)-ethyl sulfuric acid.	0
2	None	10

The data in Table I clearly shows the marked superiority of the improved hydrocarbon fuel compositions according to the present invention over a conventional diesel, jet or burner fuel. Run 1 shows that no filter deposit whatsoever is obtained from fuel oil compositions containing a representative N,N,di-(alkylbenzyl)-amino alkyl sulfuric acid, whereas the fuel oil base stock itself gives an extremely high filter deposit.

The oil compositions of the present invention were also tested for their rust-inhibiting properties. The tests were carried out in accordance with the procedure outlined in ASTM Method D665–45T. Steel spindles were immersed in an agitated distilled water and fuel oil mixture containing 0.001% by weight of additive and in an agitated sea water and fuel oil mixture containing 0.005% by weight of additive. The base stocks fuel was tested in a similar fashion. The results of these tests were as follows:

Table II

ANTI-RUST PROPERTIES

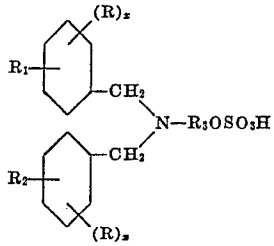
Run No.	Additive	Anti-Rust Rating	
		Distilled water-oil mixture	Sea Water-oil Mixture
1	2-[N,N,di-(dodecylbenzyl)-amino]-ethyl sulfuric acid.	No rust	No rust.
2	None	Severe rust	Severe rust.

From the above tests it will be readily observed that the improved fuel oil compositions of this invention possess remarkable rust-inhibiting properties as compared to ordinary diesel, jet or burner fuels.

The fuel oil compositions according to the present invention may contain other fuel oil additives in addition to the N,N,di-(alkylbenzyl)-amino alkyl sulfuric acid. Such additives include: lecithin; oil-soluble alkylaryl polyglycol ethers, such as didodecylphenyl dodecaethylene glycol ether; oil-soluble sulfonates, such as the lead salts of petroleum sulfonic acids containing from about 20 to 30 carbon atoms per molecule; oil-soluble naphthenates, such as the alkali metal and lead salts of petroleum naphthenic acid; alkali metal and lead salts of alkylphenyl disulfide.

We claim:

1. Oil-soluble surface-active compounds having the formula:



wherein R_1 and R_2 are alkyl groups of from 9 to 18 carbon atoms, R is a member of the group consisting of hydrogen and methyl, x is an integer of 1 to 3, and R_3 is an alkylene group of from 1 to 7 carbon atoms.

2. Compounds according to claim 1, wherein R_1 and R_2 are propylene polymers of from 9 to 18 carbon atoms.

3. Oil-soluble surface-active 2-[N,N,di-(alkylbenzyl)-amino]-ethyl sulfuric acids having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms.

4. Compounds according to claim 3, wherein the long-chain alkyl substituent on the benzene nucleus is a propylene polymer containing from 9 to 18 carbon atoms.

5. Oil-soluble surface-active 2-[N,N,di-(dodecylbenzyl)-amino]-ethyl sulfuric acid in which the dodecyl group is a propylene tetramer.

6. Oil-soluble surface-active 2-[N,N,di-(nonylbenzyl)-amino]-ethyl sulfuric acid in which the nonyl group is a propylene trimer.

7. A process which comprises heating at a temperature between about 50 and 100° C. approximately 2 molar proportions of an alkylbenzyl chloride having one alkyl group of from 9 to 18 carbon atoms and from 1 to 3 additional substituents on the benzene nucleus selected from the group consisting of hydrogen and methyl with approximately one molar proportion of an alkanolamine containing from 1 to 7 carbon atoms in the alkanol group and reacting the N,N,di-(alkylbenzyl)-alkanolamine thus obtained with a sulfating agent to produce the corresponding oil-soluble surface-active 2-[N,N,di-(alkylbenzyl)-amino]-ethyl sulfuric acid.

8. A hydrocarbon oil composition containing a small amount sufficient to inhibit line and filter clogging and corrosion of an N,N,di-(alkylbenzyl)-amino alkyl sulfuric acid having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms and an alkylene group containing from 1 to 7 carbon atoms connecting the amino and sulfuric acid groups.

9. A hydrocarbon fuel oil composition comprising a major proportion of a normally liquid hydrocarbon fuel oil and a small amount sufficient to inhibit line and filter clogging and corrosion of a 2-[N,N,di-(alkylbenzyl)-amino]-ethyl sulfuric acid, having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms.

10. A hydrocarbon fuel oil composition comprising a major proportion of a normally liquid hydrocarbon fuel oil boiling in the range of from about 175° C. to about 400° C. and from 0.001 to 0.20% by weight of a 2-[N,N,-di-(alkylbenzyl)-amino-ethyl sulfuric acid, having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms.

11. A hydrocarbon fuel oil composition as described in claim 10 wherein the normally liquid hydrocarbon fuel oil contains a substantial proportion of cracked petroleum distillate.

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