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SURFACE-ACTIVE COMPOUNDS AND FUEL COMPOSITIONS CONTAINING THEM

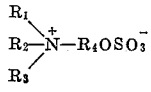
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14 Claims. (Cl. 52—0.5)

This invention concerns new and useful surface-active compounds of an ionic nature which contain both an anionic group and a cationic group within the same molecule. More particularly, the invention concerns novel surface-active compounds having an anionic sulfate group and a cationic quaternary ammonium group in a single molecule and compositions containing them.

The novel compounds of the present invention may be conveniently illustrated by the following structural formula:



wherein R_1, R_2 and R_3 represent hydrocarbon groups, at least one of which is an arylmethylene group or alkylarylmethylene group having from 1 to 24 carbon atoms in each of the alkyl radicals thereof, the remainder of said hydrocarbon groups being short-chain alkyl groups, and R_4 is an alkylene group of from 1 to 7 carbon atoms.

The above compounds are excellent surface-active agents. They are ampholytic in nature and are, therefore, capable of acting either as an acid or a base. The molecule of these surface-active compounds forms within itself a zwitterion between the quaternary nitrogen group and the alkyl sulfate group. Some of the beneficial aspects of both cationic and anionic surface-active agents are thus combined within a single compound to provide a product characterized by distinct and unusual surface-active properties not possessed by either cationic or anionic agents alone.

A further unusual feature of the surface-active compounds according to this invention is that the quaternary nitrogen group of the ampholyte is more strongly ionizable under certain conditions than an ordinary amino group would be in similar circumstances. For example, under alkaline conditions such as are often encountered in the use of surface-active agents, the compounds of this invention exhibit the characteristics of free zwitterions and may be isolated as such. On the other hand, amino sulfates under alkaline conditions do not possess free zwitterion characteristics.

The new compounds according to this invention may be either preferentially water-soluble or preferentially oil-soluble, depending upon the substituents on the aryl nucleus. A preferred group of compounds is that characterized in having two aryl groups and an alkyl group of from 9 to 18 carbon atoms on each of the aryl groups. Compounds of this latter type are preferentially oil-soluble and are useful in lubricating and fuel oil compositions.

The preferentially oil-soluble compounds which are a particularly desirable species of this invention 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 stocks 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.

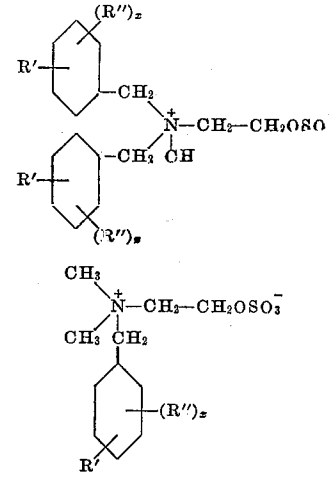
The compounds of this invention, as mentioned in connection with the above structural formula, contain at least one aryl or alkaryl group, each of which is connected by a methylene linkage to the nitrogen. Examples of suitable aryl groups are benzene, naphthalene, anthracene, toluene, xylene, mesitylene, etc., with benzene and

toluene presently preferred for their availability and the high degree of effectiveness characteristic of the compounds containing them. The alkyl substituents of the alkyl aryl methylene groups may be straight-chain or branched-chain in nature and may vary from 1 to 24 carbon atoms in length. The alkyl groups may be derived from various sources such as halogenated hydrocarbons, aliphatic alcohols, and olefins including cracked petroleum fractions, and polymers of ethylene, propylene and butylene. Propylene polymers containing from 9 to 18 and, more specifically, from 12 to 15 carbon atoms per molecule are presently preferred. Their ready availability and unusual chemical stability toward alkylating cataylsts and sulfating agents, derived apparently from their characteristically moderate chain-branching, renders them particularly suitable for present purposes.

The short-chain alkyl substituents on the quaternary nitrogren in the above structural formula also may be straight-chain or branched-chain in nature and may vary from 1 to 7 carbon atoms in length. Alkyl groups containing 1 or 2 carbon atoms are preferred, since they may be conveniently derived from dimethyl sulfate and diethyl sulfate in accordance with the preferred process for preparing these novel surface-active compounds which is described hereinafter.

The alkylene group, R_4, in the above formula likewise may be branched- or straight-chain. It may be obtained by employing any suitable alkanolamine in the preparations hereinafter disclosed. Alkylene groups of from 2 to 4 carbon atoms are preferred since they are obtainable from the ethanol, propanol and butanol amines which are desirable for their effectiveness and ready availability.

The 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates and 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates which constitute a preferred embodiment of the present invention may be illustrated by the formulae:



wherein R′ is a long-chain alkyl group of from 9 to 18 carbon atoms, R″ is a hydrogen or methyl group and x is an integer of from 1 to 3. These compounds are unusually effective dispersing agents and rust inhibitors in lubricating and fuel oil compositions.

The compounds according to the invention as illustrated by the above preferred class may be conveniently prepared by quaternizing a suitable N,N-di-(alkylbenzyl)-ethanolamine or N-alkylbenzyl ethanolamine with dimethyl sulfate as the first step. The N-alkylbenzyl ethanolamines or N,N-di-(alkylbenzyl)-ethanolamines themselves may be obtained by reacting approximately one or two molar proportions of a long-chain alkylbenzyl chloride having the desired type of alkylbenzyl group with one molar proportion of ethanolamine in the presence of a mild neutralizing agent, such as sodium bicarbonate. The N,N-di-(alkylbenzyl)-N-methyl-N-(2-hydroxyethyl)-ammonium methosulfates or N-alkylbenzyl-N,N-dimethyl-N-(2-hydroxyethyl)-ammonium methosulfates obtained in the first step may then be reacted with a sulfating agent, such as sulfuric acid or

chlorosulfonic acid, to produce the corresponding 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates and 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates of this invention. As an alternative, the compounds of this invention as illustrated by the preferred species may be prepared by first reacting approximately one or two molar proportions of a long-chain alkylbenzyl chloride with N-methyl or N,N-dimethyl ethanolamine to give the N,N-di-(alkylbenzyl-N-methyl-N-(2-hydroxyethyl)- and N-alkylbenzyl-N,N-di-methyl-N-(2-hydroxyethyl)-ammonium chlorides. These quaternaries may then be reacted with a sulfating agent to give the desired quaternary ammonium sulfates.

As a further illustration of the novel surface-active compounds of this invention and processes for preparing them, the following specific examples are offered.

Example 1.—Preparation of 2-[N-dodecylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate

A solution of 150 parts of dodecylbenzyl chloride, the dodecyl group of which was a propylene tetramer, 49 parts of N,N-dimethyl-aminoethanol and 100 parts of isopropanol was refluxed for six hours. This solution was cooled, diluted with 200 parts of water and then extracted with two 150 part portions of mixed hexane. The aqueous solution was then concentrated under reduced pressure to yield 173 parts of N-dodecylbenzyl-N,N-dimethyl-N-(2-hydroxyethyl)-ammonium chloride in the form of a viscous, yellow grease. This material, on analysis, was found to contain 3.47% nitrogen as compared to a theoretical of 3.65%.

105 parts of the N-dodecylbenzyl-N,N-dimethyl-N-(2-hydroxyethyl)-ammonium chloride prepared above was dissolved in 100 parts of chloroform and added to a solution of 79 parts of chlorosulfonic acid in 50 parts of chloroform over a period of about one hour. The addition was carried out at a temperature of 23–27° C. After the addition was complete, the reaction mixture was stirred at about 25° C. for two hours and then poured onto 100 parts of ice. The water formed was removed and discarded and the chloroform solution was neutralized with sodium hydroxide to a pH of 7.0. It was then washed with two 200 part portions of water and finally concentrated under reduced pressure to yield 86 parts of 2-[N-dodecylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate in the form of a light yellow, tacky, solid material. This material, on analysis, was found to contain 3.23% nitrogen as compared to a theoretical of 3.27% nitrogen.

Example 2.—Preparation of 2-[N,N-di-(dodecylbenzyl-N-methyl ammonium]-ethyl sulfate

14 parts of dimethyl sulfate was added portion-wise to 58 parts of N,N-di-(dodecylbenzyl)-aminoethanol in 100 parts of ethanol. The dodecyl group attached to the benzyl nucleus of the N,N-di-(dodecylbenzyl)-aminoethanol was a propylene tetramer. Following the addition, the mixture was refluxed for three hours, diluted with water and mixed hexanes and allowed to settle. The alcoholic solution was then washed with three 50 part portions of water and concentrated under reduced pressure to give 50 parts of N,N-di-(dodecylbenzyl)-N-methyl-N-(2-hydroxyethyl)-ammonium methosulfate in the form of a viscous, yellow liquid. This material on analysis gave 1.76% nitrogen as compared with a theoretical of 1.99%.

30 parts of the N,N-di-(dodecylbenzyl)-N-methyl-N-(2-hydroxyethyl)-ammonium methosulfate prepared above were dissolved in 50 parts of chloroform and added portion-wise to 12 parts of chlorosulfonic acid in 75 parts of chloroform. The addition was carried out at a temperature of 13–17° C. After the addition was complete, the reaction mixture was stirred at 15 to 20° C. for one-half hour and then poured onto 100 parts of crushed ice. The mixture was neutralized with dilute caustic solution and then allowed to settle. The aqueous portion was removed and discarded and the chloroform solution washed with water. Following this, the chloroform solution was concentrated under reduced pressure to give 25 parts of a light yellow semi-solid. This material was shown by comparison of nitrogen and sulfur analysis with theoretical to be 2-[N,N-di-(dodecylbenzyl)-N-methyl ammonium]-ethyl sulfate.

Example 3.—Preparation of 2-[N,N-di-(nonylbenzyl)-N-methyl ammonium]-ethyl sulfate

A solution of 19 parts of dimethylsulfate in 50 parts of benzene was added to 60 parts of N,N-di-(nonylbenzyl)-aminoethanol in 100 parts of benzene. The nonyl groups on the benzyl nucleus were derived from propylene trimer. After the addition, the solution was refluxed for one hour, cooled to 30° C. and treated with four parts of sodium hydroxide in 25 parts of water. The reaction mixture was then refluxed for 20 minutes with stirring, cooled, and the water layer removed and discarded. The benzene solution was then washed with two 50 part portions of water and concentrated under reduced pressure to yield the N,N-di-(nonylbenzyl)-N-methyl-N-(2-hydroxyethyl)-ammonium methosulfate in the form of a light amber color viscous liquid.

56 parts of the N,N-di-(nonylbenzyl)-N-methyl-N-(2-hydroxyethyl)-ammonium methosulfate prepared above were dissolved in chloroform and added to 21 parts of chlorosulfonic acid also in chloroform. The addition was made in increments at a temperature of 13–17° C. After the addition was complete, the reaction mixture was stirred at 15–20° C. for one-half hour and poured onto 100 parts of crushed ice as in the preceding example. After neutralization with dilute caustic settling and removal of the aqueous portion, the chloroform solution was washed with water and concentrated under reduced pressure. 32 parts of an amber, tacky solid were thus obtained which was shown by nitrogen and sulfur analysis to be 2-[N,N-di-(nonylbenzyl)-N-methyl ammonium]-ethyl sulfate.

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

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

In the production of hydrocarbon fuels 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. When employed in burner fuels, diesel engine fuels, and jet fuels these stocks 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, 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 gum and sludge in hydrocarbon fuels containing cracked stocks and also causes rusting of exposed ferrous metal surfaces, which rust in turn eventually loosens and also contributes to the clogging of filters and lines.

As a part of the present invention, it has been discovered that by the addition of a small amount of the 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-alkyl sulfates of 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-alkyl sulfates described above to normally liquid hydrocarbon fuels, 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 the fuel oil system.

Suitable hydrocarbon fuel base stocks 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 to 400° C. Such distillates are ordinarily characterized by an A. P. I. gravity of at least 20° and usually at least 25°. The base stocks 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. With 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 2-[N,N-di-(alkylbenzyl)-N-methyl-ammonium]-alkyl sulfates and 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-alkyl sulfates, 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 fuel oil 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 evalution 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 fuel tests using regular fuel oil burners and jet and diesel engines. The test is carried out by mixing 500 ml. of a fuel composition containing 0.01% by weight of the additive with 500 ml. of water containing 102 parts per million hardness calculated as calcium and magnesium carbonates, 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 a opaque cuff at their interface. This interface cuff is then filtered through a fritted glass crucible with the aid of a vacuum. Only as much oil and water 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 thereon is used as a comparative measure of the hydrocarbon fuels' 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 tendency. The standard filters are numbered 0 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 amount of filter deposit.

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 fuel of the burner, diesel or jet type. The base fuel employed in each case was a mixture of equal parts of straight-run distillate from a waxy base crude falling in the range of from 196° C. to 357° C. and a Thermofor catalytic cracked fraction boiling in the range of from 191° C. to 297° C.

TABLE I.—INTERFACE FILTER DEPOSIT RATING

Run No.	Additive	IFD No.
1	2-[N,N-di-(dodecylbenzyl)-N-methyl ammonium]-ethyl sulfate.	0
2	2-[N,N-di-(nonylbenzyl)-N-methyl ammonium]-ethyl sulfate.	1
3	2-[N-dodecylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate.	0
4	None	10

The data in Table I above clearly show the marked superiority of the improved hydrocarbon fuel compositions according to the present invention over a conventional burner, diesel or jet fuel. Runs 1, 2 and 3 each shows that very little or no filter deposit is obtained from fuel oil compositions containing representative 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates or 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates of this invention. On the other hand, the fuel oil base stock by itself as shown by run 4 gives an extremely high filter deposit.

The 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 D–665–47T. 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 stock fuel without additive was tested in a similar fashion. The results of these tests were as follows:

TABLE II.—ANTI-RUST PROPERTIES

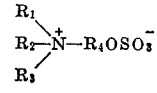
Run No.	Additive	Anti-rust Rating	
		Distilled water-oil mixture	Sea water-oil mixture
1	2-[N,N-di-(dodecylbenzyl)-N-methyl ammonium]-ethyl sulfate.	No rust	No rust.
2	2-[N,N-di-(nonylbenzyl)-N-methyl ammonium]-ethyl sulfate.	do	Do.
3	2-[N-dodecylbenzyl-N,N-di-methyl ammonium]-ethyl sulfate.	Light rust	Light rust.
4	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 with ordinary burner, diesel or jet fuels.

The fuel oil compositions according to the present invention may contain other fuel oil additives in addition to the 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates and 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates. 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 acid containing from about 20 to 30 carbon atoms per molecule; oil-soluble naphthenates such as the alkali metal and lead salts of petroleum naphthenic acids; alkali metal and lead salts of alkyl phenol disulfide.

We claim:

1. Compounds of the formula:



wherein R_1, R_2 and R_3 are hydrocarbon groups, at least one of which is an alkyl aryl methylene group containing from 1 to 24 carbon atoms in the alkyl portion thereof, the remainder of said hydrocarbon groups being short-chain alkyl groups and R_4 is an alkylene group of from 1 to 7 carbon atoms.

2. 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms.

3. 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates having a long-chain alkyl substituent on the benzene nucleus containing from 9 to 18 carbon atoms.

4. 2-[N,N-di-(dodecylbenzyl)-N-methyl ammonium]-ethyl sulfate wherein the dodecyl group is a propylene polymer.

5. 2-[N,N-di-(nonylbenzyl)-N-methyl ammonium]-ethyl sulfate wherein the nonyl group is a propylene polymer.

6. 2-[N-dodecylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate wherein the dodecyl group is a propylene polymer.

7. A process which comprises refluxing approximately 2 molar proportions of a long-chain alkylbenzyl chloride having from 9 to 18 carbon atoms in the long-chain alkyl portion thereof with approximately 1 molar proportion of ethanolamine in the presence of sodium bicarbonate, quaternizing the di-(alkylbenzyl)-ethanolamine thus obtained with dimethyl sulfate and reacting the quaternary ammonium methosulfate product therefrom with a sulfating agent to give oil-soluble, surface-active 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates having from 9 to 18 carbon atoms in the long-chain alkyl substituent on the benzene nucleus.

8. A hydrocarbon oil composition containing a small amount sufficient to inhibit line and filter clogging and corrosion of a member of the group consisting of 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates and 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfates having a long-chain alkyl substituent of from 9 to 18 carbon atoms on the benzene nucleus.

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 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfates having a long-chain alkyl substituent of from 9 to 18 carbon atoms on the benzene nucleus.

10. 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 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate having a long-chain alkyl substituent of from 9 to 18 carbon atoms on the benzene nucleus.

11. 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 2-[N,N-di-(alkylbenzyl)-N-methyl ammonium]-ethyl sulfate having a long-chain alkyl substituent of from 9 to 18 carbon atoms on the benzene nucleus.

12. 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 2-[N-alkylbenzyl-N,N-dimethyl ammonium]-ethyl sulfate having a long-chain alkyl substituent of from 9 to 18 carbon atoms on the benzene nucleus.

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

14. A hydrocarbon fuel oil composition as described in claim 12, wherein the normally liquid hydrocarbon fuel oil contains a substantial proportion of cracked petroleum distillate.

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