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3,711,408

SULFONAMIDES OF HIGH MOLECULAR WEIGHT ALKYL-SUBSTITUTED BENZENE SULFONIC ACIDS AND THEIR PREPARATION

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7 Claims 10

ABSTRACT OF THE DISCLOSURE

Polymethylene-containing sulfonamides of alkyl substituted benzene sulfonic acids whose alkyl-substituent has a molecular weight in the range of 400 to 2800 are oil soluble, impart thermally stable dispersancy to oil solutions of the sulfonamides. The sulfonamides are preferably of polymethylene-containing diprimary amines such as polyazalkylene diamine, polymethylene diamine, polyethylene imines of 1000–40,000 molecular weight and di(aminopolymethylene) piperazine. The sulfonamides are conveniently prepared as solutes in light mineral oil (white oil to SAE 10 type hydrocarbon oil) by reaction of suitable alkylbenzene sulfonic acid chloride and the polymethylene-containing diprimary amine in the presence of pyridine and C₅–C₈ alkane, removing the alkane and pyridine, treating the residue with a light mineral oil suspension of calcium hydroxide and filtering the resulting mixture.

BACKGROUND OF THE INVENTION

Sulfonamides are known to possess chemical and physical stability. Sulfonamides of benzene and alkylbenzene sulfonic acids previously known, while soluble in hydrocarbon oils, have not had sufficient oil solubility or stability to make them generally attractive as addition agents for lubricating oil formulations, especially as primary detergent or dispersant addition agents for said formulations. Rather the previously known sulfonamides have found some secondary use in lubricant formulations as anti-rust and anti-corrosion agents.

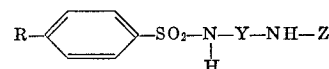
U.S. Pat. No. 2,660,562 discloses guanidine salts of alkyl, alkylaryl and petroleum sulfonic acids (mahogany acids) as gelling agents for grease preparation, anti-rust agents for oils and detergents for oils. For grease gelling agents the alkyl content of the sulfonic acid-guanidine salt should have 17–35 carbon atoms, for anti-rust agents have up to 40 carbon atoms and for detergency agents must have 40 to 70 carbon atoms. Thus for said detergency use of guanidine salt has in its alkylbenzene moiety an alkyl group of about 560–980 molecular weight. Such guanidine salts were derived from guanidine, or its carbonate, methyl guanidine, mono- and diphenyl guanidine, wax-alkyl-substituted guanidines, chloroguanidine, and phenyl biguanidine; by their reaction with the sulfonic acid having 40–70 carbon atoms in their alkyl chain. Which such C₄₀–C₇₀ alkyl containing salts had a sufficiently large alkyl group to impart suitable oil-solubility, the character and nature of the guanidine moiety were small when compared to the moiety contributed by the sulfonic acid. That patent establishes that such guanidine salts as acceptably useful lubricant oil detergents for the severity use required at the time (about 1950–51) that said invention was made. One basis for use acceptance was the diesel engine CRC L–1 Test (using modified H2-Lauson engine) in which an alkaline earth metal salt of alkylphenol sulfide would give a passing detergent rating. However, as time has gone by the in-service detergency requirements for diesel engine

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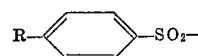
crankcase lubricating oils have increased and said diesel engine L–1 Test (rather low temperature severity) has been successively superseded by 1–D Test, then by 1–G Test and finally by Caterpillar-1H Test which is far more severe with respect to operating temperature and oil environment during the test. Oils containing said guanidine salts, while given a passing rating in the CRC–L1 Test would not pass the much more severe Caterpillar-1H Test.

SUMMARY OF INVENTION

We have discovered a novel class of lubricant oil-soluble alkylbenzene sulfonamides whose amide moiety with respect to the alkylbenzene sulfonic acid moiety is larger and different than the same relationship of guanidine moiety to alkylbenzenesulfonic acid in the prior guanidine salts. Hence the novel sulfonamides provide detergency-dispersancy properties in lubricating oils that advantageously meet more severe requirements of the diesel engine Caterpillar-1H Test. The novel sulfonamides have high molecular weight nuclear alkyl-substituent on the benzene ring. Preferably said nuclear alkyl-substituent has a molecular weight in the range of 400 to 2800 and most preferred of these are the nuclear polypropyl and polybutyl substituents of number average molecular weight ($\bar{M}_n$) in the range of 400–2800. The amide moiety of the sulfonamide is derived from polymethyl-containing two primary amine groups which include the types polymethylene diamine, polyazamethylene diamines, di(aminopolymethylene) piperazine and polyethylene imine $\bar{M}_n$ 600–40,000. Such novel sulfonamides are mono- and disulfonamides having the formula:



wherein R is the alkyl substituent of 400–2800 $\bar{M}_n$, Y is the polymethylene containing moiety of the diprimary-amine and Z is hydrogen (mono-sulfonamide) or



(disulfonamide) wherein R is the 400–2800 $\bar{M}_n$ substituent.

This preparation of alkylbenzene sulfonamides by reaction of an amine with alkylbenzene sulfonic acid is somewhat unsatisfactory because amine salt formation is favored and substantial energy is required to convert the salt to amide through the removal of one oxygen atom from the sulfur atom.

We have found that the preparation of the present inventive alkylbenzene sulfonamide products can overcome those drawbacks by reacting alkylbenzene sulfonic acid chloride with the polymethylene containing diprimary amine in the presence of a C₅–C₈ alkane reaction diluent and pyridine as hydrogen chloride acceptor, removing both alkane and pyridine by evaporation or distillation, treating the residue with a light oil (white oil to SAE 10 hydrocarbon oil) suspension of calcium hydroxide in an amount equivalent to the alkylbenzene sulfonic acid chloride, and then filtering the resulting mixture to remove calcium chloride. In this way alkylbenzene sulfonic acid chloride does not bring in unwanted impurities and by-product water does not have to be driven off from a liquid product. Although pyridine is initially used as HCl acceptor, distillation or evaporation removal of pyridine does not remove by-product HCl. This by-product is removed as solid calcium chloride.

The monosulfonamide is obtained by using alkylbenzene sulfonic acid chloride and polymethylene-containing diprimary amine in the respective reactant molar ratio of 1.0:1.0 and in the respective reactant molar ratio of 2.0:1.0

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for disulfonamide preparation. For each mole of alkylbenzene sulfonic acid chloride used there is produced 1.0 mole HCl. To convert HCl to CaCl_2 there is used one equivalent (0.5 mole) of calcium hydroxide. Thus the amount of $\text{Ca}(\text{OH})_2$ used (0.5 to 1.0 mole) is equivalent to the 1.0 to 2.0 moles alkylbenzene sulfonic acid chloride, since 1.0 mole of $\text{Ca}(\text{OH})_2$ represents two equivalents with respect to 1.0 mole of HCl.

The alkylbenzene sulfonic acid chloride is conveniently obtained for said sulfonamide preparative method by ambient temperature (75–80° F.) sulfochlorination of the appropriate alkylbenzene by either of the following two reactions in the presence of C_5 to C_8 alkane for good physical contact of reactants. An equal molecular portion of sulfonyl chloride (SO_2Cl_2) and chlorosulfonic acid



is used as chlorosulfonation agent to chlorosulfonate and alkylbenzene. The chlorosulfonation reaction on alkylbenzene is carried out with 1.0 mole of said chlorosulfonation agent per mole alkylbenzene. In place of said chlorosulfonation agent chlorosulfonic acid (ClSO_3H) can be used in the ratio of two moles thereof per mole of alkylbenzene, the sulfuric acid sludge, which then upon addition of water to 85–87% H_2SO_4 , readily settles out of the quiescent mixture and is easily and completely removed. The alkane solution of reasonably pure alkylbenzene sulfonic acid chloride is then used for the sulfonamide preparation before described.

EMBODIMENTS OF INVENTION

The alkylbenzene sulfonic acid chloride reactant has been before well defined with respect to the size of its nuclear alkyl substituent. The alkyl substituent can be derived from any appropriate source when preparing the alkylbenzene for use in chlorosulfonation. Thus the alkylbenzene can be obtained by alkylation of benzene with any suitable alcohol, olefin or alkyl halide whose hydrocarbon portion has the requisite 400–2800 molecular weight. Advantageously the hydrocarbon alkylating agent is a liquid viscous polypropylene or polybutene of $\overline{M}_n$ 400–2800 obtained by AlCl_3 catalyzed polymerization respectively of propylene or butene such as isobutylene, butene-1, butene-2 and mixtures thereof and mixtures of butane, butene-1, butene-2 and isobutylene with or without small amounts of butadiene present. Such liquid polypropylene and polybutene and their preparation are well known.

The C_5 – C_8 alkane reaction diluent used in chlorosulfonation and in the sulfonamide preparation are the pentanes, hexanes, heptanes and octanes both normal and branched chain as well as mixtures of normal and branched chain isomers.

The polymethylene-containing diprimary amines include polymethylene diamines of 2 to 10 methylene groups such as ethylene diamine; 1,2- and 1,3-propylene diamine; 1,2-, 1,3- and 1,4-butylene diamine; 1,2-, 1,3-, 1,4- and 1,5-pentylene diamines; 1,2- to 1,6-hexylene diamines; 1,2- to 1,7-heptylene diamines; 1,2- to 1,8-octylene diamines; 1,2- to 1,9-nonylene diamines and 1,2- to 1,10-decylene diamines and their branched isomers. Polyazamethylene diamines are polymethylene-containing diprimary amines and illustrative thereof are the alkylene polyamines; e.g. ethylene, propylene, butylene, etc. polyamines; obtained by reacting a C_2 to C_{10} alkylene dichloride with ammonia. Of the preferred alkylene polyamines (therefore also of the polyazamethylene diprimary amine) are ethylene polyamines: $\text{H}_2\text{N}-(\text{C}_2\text{H}_4\text{NH})_x-\text{H}$ wherein x is a number of from 2 to 10. The polyethylene imines of 600–40,000 $\overline{M}_n$ are a well known class of compounds and are a type of polymethylene-containing diprimary amine within the understanding of this invention. The remaining type of useful polymethylene-containing diprimary amines useful in providing the amide moiety of the present inventive sulfonamide compounds are di(aminopolymethylene) piperazine whose aminopolymethylene

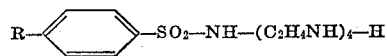
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groups are aminoethyl, aminopropyl, aminobutyl, aminopentyl, aminoheptyl, aminoheptyl, aminoheptyl, aminononyl and aminodecyl groups, that is $\text{H}_2\text{N}-(\text{CH}_2)_x$ groups wherein x is a number from 2 to 10.

The novel inventive sulfonamides and their preparation are further described and illustrated by the following examples.

EXAMPLE 1

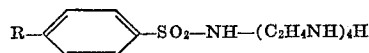
There are combined and stirred in a reaction vessel having a reflux condenser 0.84 moles of alkylbenzene sulfonic acid chloride whose alkyl group has 400 $\overline{M}_n$ and 1000 milliliters of heptane until a solution forms. To the stirred solution is slowly added 0.84 mole tetraethylene pentamine admixed with 89 grams of pyridine to maintain a temperature of 200° F. maximum. Thereafter the mixture is heated to reflux temperature of heptane (about 208–210° F.) for 20 minutes and then heptane and pyridine were distilled out of the reaction mixture. A slurry of 31 grams of calcium hydroxide in 730 grams of SAE 5W oil are added and the hot mixture is filtered to remove calcium chloride. The filtrate contains about 50 weight percent of monosulfonamide shown below and about 4% nitrogen by weight. Said monosulfonamide has the formula



where R is 400 $\overline{M}_n$ alkyl.

EXAMPLE 2

The process of Example 1 is repeated except that the alkylbenzenesulfonic acid chloride has as its alkyl-substituent a polypropyl group of 729 $\overline{M}_n$ and the slurry of 31 grams calcium hydroxide had only 113 grams of SAE 5W oil. The filtrate is obtained at 210° F. and contains 80.6% monosulfonamide and 2.35% nitrogen on weight basis. The monosulfonamide has the formula



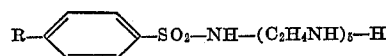
wherein R is a polypropyl of 729 $\overline{M}_n$.

EXAMPLE 3

A sulfonamide is prepared by reacting 1 mole of alkylbenzene sulfonic acid chloride (alkyl-substituent is $\overline{M}_n$ 729 polypropyl group) dissolved in 500 grams of hexane with 0.015 mole of poly(ethyleneimine) of 20,000 $\overline{M}_n$ in the presence of 200 ccs. of pyridine at a temperature of 180° F. or hexane reflux. Following removal of hexane and pyridine by evaporation, the residue is treated with a slurry of 56 grams calcium oxide in 800 grams of SAE 5W oil with stirring at a temperature of 300° F. The hot mixture is filtered. The filtrate contains 50 weight percent of the resulting sulfonamide of poly(ethyleneimine) and has a nitrogen content of 4–5 percent by weight.

EXAMPLE 4

The preparative method of Example 2 is repeated except that pentaethylene hexamine is substituted for tetraethylene pentamine. The filtrate contains on a weight basis about 80% monosulfonamide of the formula



wherein R is polypropyl of 729 $\overline{M}_n$, and 2.7% nitrogen.

EXAMPLE 5

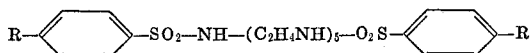
The preparative method of Example 2 is repeated using 1 mole of alkylbenzene sulfonic acid chloride (alkyl is 729 $\overline{M}_n$ polypropyl) dissolved in 800 grams hexane and 0.5 mole of poly(ethyleneimine) of 600 $\overline{M}_n$. Following removal of hexane and pyridine, the residue is treated with a slurry of 56 grams calcium hydroxide in 600 ccs. SAE 5W oil with stirring at 300° F. The hot filtrate contains the alkyl(polypropyl 729 $\overline{M}_n$ substituted benzene sul-

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fonamide of said 600 $\overline{M}_n$ poly(ethyleneimine) in a concentration of 48.5 weight percent ~4% nitrogen.

EXAMPLE 6

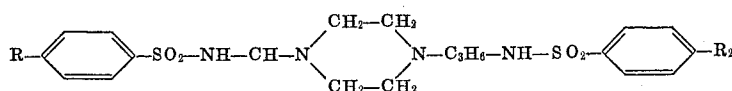
The preparative method of Example 4 is repeated except the mole ratio of alkyl(polypropyl of 729 $\overline{M}_n$)-substituted benzene sulfonic acid chloride to pentaethylene hexamine is 2.0:1.0. The hot filtrate contains on a weight basis 68% of the disulfonamide of the formula:



wherein each R is polypropyl of 729 $\overline{M}_n$, and 2% nitrogen.

EXAMPLE 7

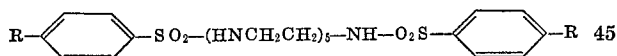
There is prepared the disulfonamide of the formula:



by reacting equivalent molar proportions of alkyl(polybutyl of 2000 $\overline{M}_n$)-substituted benzene sulfonic acid chloride and 2,6-di(aminopropyl)piperazine in the presence of hexane to dissolve the sulfonic acid chloride and pyridine. Following removal of hexane and pyridine by distillation, the residue is treated by adding and stirring a slurry of calcium hydroxide in SAE 5W oil to provide on a weight basis 40% of the above disulfonamide wherein R is polybutyl of 2000 $\overline{M}_n$. The hot filtrate obtained after removal of CaCl_2 contains 0.5% nitrogen on a weight basis.

EXAMPLE 8

The preparative method of Example 7 is repeated using a 2.0:1.0 mole of alkyl (polypropyl of 729 $\overline{M}_n$ -substituted benzene sulfonic acid chloride to pentaethylenehexamine. The slurry of calcium hydroxide is adjusted to provide 2.0 equivalents of calcium per 2.0 moles of alkylbenzene sulfonic acid and the SAE 5W oil is adjusted to provide a 40 weight percent concentration of the disulfonamide of the formula:



wherein each R is 729 $\overline{M}_n$ polypropyl. The hot filtrate contains 1.7% nitrogen by weight.

Two lubricant oil formulations are prepared for testing as crankcase lubricating oils using alkylbenzene sulfonamides of this invention to demonstrate their utility. These formulations and their ingredients on a volume basis are:

FORMULATION A

Ingredient:	Volume percent
SAE 20 oil	60.3
SAE 40 oil	32.0
Oil solution from Example 2	4.5
Oil solution zinc dialkyldithiophosphate	0.7
Oil solution calcium alkylbenzene sulfonate	1.5
Pour point depressant	1.0
Total	100.0

FORMULATION B

Ingredient:	Volume percent
SAE 5W oil	37.15
SAE 10 oil	47.00
Viscosity index improver	7.75
Oil solution of Example 8	5.00
Oil solution zinc dialkyldithiophosphate	1.10
Oil solution of calcium alkylbenzene sulfonate	2.00
Total	100.00

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In each of Formulations A and B the zinc dialkyldithiophosphate has primary alkyl groups and the solution contains 40 weight percent of the zinc salt. Also the calcium sulfonate solution contains 40 weight percent of calcium salt.

Formulation A was tested as crankcase lubricating oil in a diesel engine operated under the standardized Caterpillar-1H Test conditions for 240 hours. Examination and evaluation of the pistons after said test showed top ring groove failing of 15%, second ring groove had trace of carbon, third and fourth ring grooves clean, first land had 5% light lacquer, second and third lands clean and a brown lacquer under crown deposit.

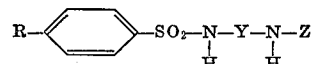
Formulation B was tested in a 289 cubic inch V-8 engine of Ford Motor Company under the standardized 289 Ford sequence V B Test operation conditions for

192 hours. Results of this test made after conducting said test and inspection of engine parts were:

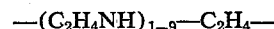
Total varnish (basis 50=clean)	34.1
Oil pump relief valve (10=clean)	9.8
Valve lifters sticking	0
Plugging of oil screen	0
Total sludge (basis 50=clean)	37.8
Oil rings plugging (50% acceptable) percent	2
Piston rings sticking	0
Blow-by average (ft. ³ /hr.)	152.8
Percent PVC plugging:	
192 hours (at 4 inch Hg)	7.6
192 hours (at 18 inch Hg)	25

What is claimed is:

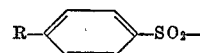
1. A composition comprising a light hydrocarbon oil solution containing 40-80 weight percent of said composition of the sulfonamide of high molecular weight alkyl-substituted benzenesulfonic acid which sulfonamide has the formula:



wherein R is the alkyl-substituent and has a molecular weight in the range of 400 to 2800; Y is polymethylene having 2 to 10 methylene groups, polyethylene imine having $\overline{M}_n$ in the range of 600-40,000, polyazethylene having the formula



or N,N'-di(polymethylene) piperazinyll whose polymethylene groups contain from 2 to 10 methylene units; and Z is hydrogen or the

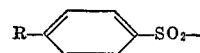


group in said formula.

2. The composition of claim 1 wherein R in the formula is polypropyl or polybutyl having $\overline{M}_n$ in the range of 400 to 2800.

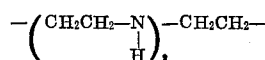
3. The composition of claim 2 wherein Z in the formula is hydrogen.

4. The composition of claim 2 wherein Z is



and said R is polypropyl or polybutyl of $\overline{M}_n$ 400 to 2800.

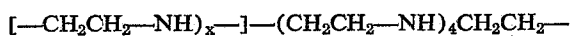
5. The composition of claim 2 wherein said formula Y is



Z is hydrogen and R is polypropyl of 729 $\overline{M}_n$.

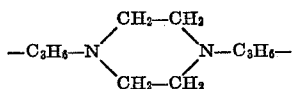
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6. The composition of claim 4 wherein said formula Y is polyazamethylene of the formula



and wherein both R groups are polypropyl of 729 $\overline{M}_n$.

7. The composition of claim 4 wherein said formula Y is group



and both R groups are polypropyl of 729 $\overline{M}_n$.

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