

UNITED STATES PATENT OFFICE

2,624,742

ALKYL THIOPHENE SULFONATE
DETERGENTSCarl B. Linn, Riverside, Ill., assignor to Universal
Oil Products Company, Chicago, Ill., a corpo-
ration of DelawareNo Drawing. Application August 23, 1947,
Serial No. 770,333

3 Claims. (Cl. 260—329)

1

The present invention relates to a process for producing compounds having surface activity in an aqueous solution thereof, said compounds being characterized broadly as alkyl thiophene sulfonate salts. The invention is more particularly concerned with the production of alkyl thiophene sulfonates which have a particular type of surface activity which renders said compounds useful for detergent purposes in laundering, toilet, and other deterging applications.

The prior art has generally recognized that certain sulfonic acids and their salts, the sulfonates, possess surface active properties in an aqueous solution thereof and such products have been made the basis of a large industry to supply non-soap detergents having deterging qualities. In many instances the synthetic type of detergents has been found to be superior to the well known soap detergents. The superiority of the sulfonate non-soap detergents is especially pronounced when the detergents are utilized in hard waters containing calcium and magnesium ions in solution. In the case of the fatty acid soaps a portion of the soap added to the water, equivalent to the amount of calcium and magnesium ions in solution in the hard water, is wasted in forming a non-active, insoluble soap curd comprising the calcium and/or magnesium fatty acid salts formed by a double displacement reaction upon addition of the soap to the hard water. In contrast to this action, the synthetic non-soap detergents of the sulfate or sulfonate salt type are stable in the presence of calcium and magnesium ions, do not react with the hard water to form an insoluble curd and therefore are effective even when added in small quantities to the water in amounts less than that which is equivalent to the quantity of calcium and magnesium ions in solution. The sulfonate salt type of detergent produced by the prior art generally employs a hydrocarbon starting material usually derived from a petroleum source, such as an aromatic hydrocarbon containing one or more short or long chain alkyl substituents or an aliphatic hydrocarbon which when sulfonated and subsequently neutralized forms the corresponding sulfonate detergent salt. Other detergent types of the sulfonate class of materials include the sulfate or sulfonate salts prepared from certain long chain alcohols and phenols, from the long chain alkanolic acids, such as the salts of the sulfonated fatty acid series and from the fatty acid glyceride esters derived from oils of vegetable or animal origin. The detergent product of the present invention produced by the

2

process hereinafter described utilizes a new class of starting materials and is characterized as the sulfonate salt of an alkyl thiophene derivative containing at least one alkyl group having from about 9 to about 20 carbon atoms per group. The desired product herein described as an alkyl thiophene sulfonate is particularly useful as a soap substitute, especially when used as a detergent in hard waters where fatty acid soaps do not give satisfactory results. One of the latter alkyl thiophene sulfonate types of detergents herein specified which possesses generally excellent qualities for detergent purposes are those compounds characterized as having a thiophene nucleus, a sulfonic acid or sulfonate salt substituent attached to said thiophene nucleus and one or more alkyl radicals also attached thereto as nuclear substituents. Preferably, one, but no more than one of said alkyl substituents has a chain length corresponding to at least a nonyl radical, but of no greater chain length than an eicosanyl radical. The detergent compound may also consist of a thiophene nucleus substituted with either one or two alkyl radicals other than the single long chain alkyl group, but when such compounds are utilized, said other alkyl groups are desirably of fewer than 5 carbon atoms per group and preferably are either methyl or ethyl groups. The process provided herein and hereinafter specified, whereby the above desired products are formed, comprises the steps: alkylating a thiophene compound (which may contain as substituents said short chain alkyl groups, when the latter are desired in the ultimate detergent product) with an alkylating agent containing an organic radical having the desired long chain alkyl group containing from about 9 to about 18 carbon atoms. The resultant product or selected fractions thereof is thereafter sulfonated with a suitable sulfonating agent and the sulfonic acid resulting therefrom neutralized to form the finished alkyl thiophene sulfonate salt comprising the present detergent.

It is a principal object of the present invention to provide a combination alkylation, sulfonation and neutralization process for producing alkyl thiophene sulfonate compounds which are useful as detergents.

Another object of the invention is to provide a combined alkylation-sulfonation process for producing alkyl thiophene sulfonic acids in high yields employing a procedure in which little or no decomposition of the thiophene starting material occurs.

In accordance with one of its embodiments, the

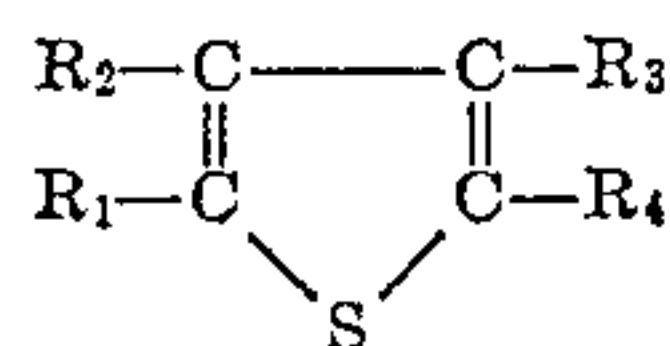
3

present invention comprises alkylating thiophene with a mono-olefinic alkylating agent containing from about 9 to about 18 carbon atoms per molecule, separating a desired thiophene alkylate from the alkylation reaction products, sulfonating said alkylate to form the corresponding alkyl thiophene sulfonic acids and neutralizing the latter sulfonic acids to form the desired product comprising the sulfonate salt derivative of an alkyl thiophene.

A more specific embodiment of the invention relates to a process for producing alkyl thiophene sulfonates wherein little or no decomposition of the thiophene reactant occurs which process comprises alkylating a thiophene compound containing at least 2 replaceable nuclear substituents with an olefinic hydrocarbon fraction containing mono-olefinic compounds having from about 9 to about 18 carbon atoms per molecule in the presence of boron trifluoride hydrate as alkylation catalyst, separating a thiophene alkylate from the alkylation products which contains an alkyl group having from about 9 to about 18 carbon atoms therein, sulfonating said alkylate in the presence of a diluent consisting of a solvent for said thiophene alkylate which is inert to the sulfonating agent, utilizing therefor as sulfonating agent a dilute sulfuric acid containing more than about 75% sulfuric acid but less than about 100% sulfuric acid, separating an alkyl thiophene sulfonic acid resulting from said sulfonation from the bulk of the excess sulfonating agent and neutralizing the separated sulfonic acid with dilute caustic to form an aqueous solution from which the detergent product may be recovered.

Other objects and embodiments of the process herein provided will be hereinafter referred to in greater detail in the following further description of the invention.

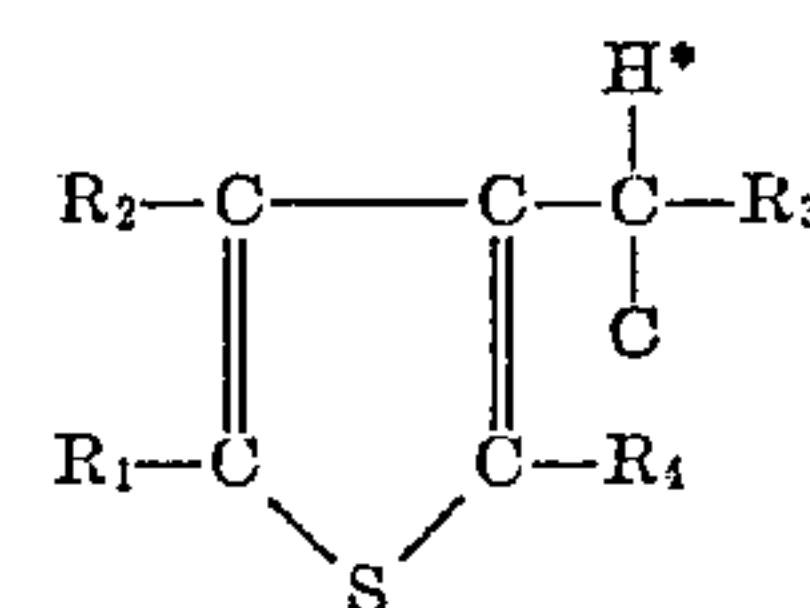
The reactant herein specified as the thiophene charging stock which in its preferred structure contains at least two nuclear substituents replaceable by an alkyl group containing from about 9 to about 18 carbon atoms per group and a further substituent replaceable by a sulfonate salt radical is a heterocyclic organic compound, the cyclic nucleus of which contains 4 carbon atoms and one sulfur atom, at least 2 of which nuclear carbon atoms contain substitutable hydrogen atoms attached thereto. The various thiophene compounds of the above preferred type which may be utilized as starting materials or charging stocks in the present process may be represented by the formula:



in which preferably at least 2 of the radicals R_1 , R_2 , R_3 and R_4 are hydrogen atoms and the other members thereof are selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, naphthyl and naphthenyl or (cycloalkyl) radicals. The preferred starting material is thiophene itself or an alkyl thiophene containing no more than 2 short chain alkyl groups each of which contains no more than about 5 carbon atoms per group, represented by such compounds as methyl thiophene, dimethyl thiophene, ethyl thiophene, diethyl thiophene, etc. up to about the diamyl derivative. It has been observed that when starting materials having alkyl groups containing more than about 5 carbon atoms per alkyl group are utilized, the resultant

4

products progressively decrease in detergency as the length of the alkyl group increases beyond 5 carbon atoms. Although compounds of the above type, containing at least two nuclearly replaceable hydrogen atoms are generally preferred herein as starting materials in the present process, another type of thiophene compound also utilizable herein as the thiophene reactant is represented by the above formula in which R_1 , R_2 , R_3 and R_4 are alkyl, aryl, aralkyl, naphthyl or naphthenyl groups, but at least one of said groups is an alkyl or an aralkyl group containing a secondary carbon atom in the alkyl side-chain attached to the thiophene nucleus, said carbon atom containing an active hydrogen atom attached thereto which is replaceable during the alkylation reaction herein provided by an alkyl group, containing from about 9 to about 18 carbon atoms per group. A typical structural formula of the latter class of thiophene reactants may be represented by the following



wherein R_1 , R_2 , R_3 and R_4 are selected from the group consisting of hydrogen, alkyl aryl, aralkyl, naphthyl, and naphthenyl radicals and where H^* is an active hydrogen atom replaceable during alkylation, by an alkyl group containing from about 9 to about 18 carbon atoms per group. In the subsequent sulfonation stage of the process, R_3 is replaceable by the sulfonic acid radical to form the detergent or detergent intermediate.

The alkylating agents which comprises the other primary reactant in the alkylation reaction is characterized generally as an organic compound capable of yielding an alkyl radical in which from about 9 to about 18 carbon atoms are present and which is capable of condensing during the alkylation reaction and under the reaction conditions specified for alkylation with the thiophene reactant to yield the corresponding alkyl thiophene compounds. Organic compounds utilizable as alkylating agents in the present process include mono-olefins having a relatively straight chain configuration, mineral acid esters, such as the alkyl halides, and alkoxy compounds of the class consisting of aliphatic alcohols, ethers and esters of carboxylic acids in which the alkyl portion of the molecule, transferred to the thiophene reactant during the alkylation reaction, contains from about 9 to about 18 carbon atoms. The above various alkylating agents have the property of producing alkyl groups as intermediates or at least as transient intermediates during the course of the condensation reaction which results in the formation of the thiophene alkylate. The alkylating agents hereinabove mentioned are not to be regarded as equivalents and reaction conditions must be adjusted to correspond to the reactivity of the various types of compounds specified above. Alkyl halides containing a straight chain configuration and the desired number of carbon atoms, such as a mono chlorinated kerosene fraction boiling from about 180° to about 260° C., constitute one of the preferred alkylating agents, especially when utilized in an alkylation reaction in which a metal halide alkylation catalyst is employed. The preferred alkylating agents in the present process are the mono-olefins con-

taining from about 12 to about 18 carbon atoms per molecule. These may be obtained from any source, as, for example, by the polymerization of propylene, butylenes, etc. or said olefins may be specific fractions of cracked petroleum distillates such as the higher boiling fractions of cracked gasoline and other olefinic distillates boiling generally from about 160° to about 240° C. The olefin polymers produced by polymerization of propylene, and/or the butylenes, and other olefins, as for example, a propylene tetramer fraction, may readily be obtained by contacting the olefin monomer or a mixture thereof with other olefins at polymerization conditions with a polymerizing catalyst such as a calcined composite of a siliceous carrier and a phosphoric acid, known generally in the art as a "solid phosphoric acid" catalyst.

Catalysts utilizable in the alkylation stage of the present process to effect the transfer of the alkyl radical of the alkylating agent to the thiophene reactant include the relatively large group of catalysts employed by the art for alkylation reactions and referred to generally herein as alkylation catalysts. Within this group are included the Friedel-Crafts type halides, particularly the chlorides and bromides of metals such as tin (stannic), aluminum, iron (ferric), zinc, bismuth, zirconium, and antimony and of the Friedel-Crafts non-metallic halide, boron trifluoride. These catalysts are sometimes utilized in substantially anhydrous conditions, either as a free halide or deposited upon carrying or spacing material such as kieselguhr, silica gel, brick, etc. and are preferably contacted with the reactants in the presence of a promoter such as hydrogen chloride and hydrogen bromide. In the case of some of the above catalysts, for example, boron trifluoride, it is preferable that the catalyst be modified by union with water, alcohols, and the like to form complexes. The hydrated catalysts are represented by salts such as $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, which is a particularly effective catalyst and is therefore one of the preferred catalysts in the present process. Other complexes of this type having an alkylating ability may be formed, for example by combining in required stoichiometric amounts the Friedel-Crafts halide, such as aluminum chloride or boron trifluoride, with the oxygen-containing organic compound, such as an ether (diethylether, for example) at a reaction temperature which may vary within the range of from about -20° to about 70° C. Other oxygen, containing organic compounds which may be employed in the preparation of the complex catalyst include alcohols, such as methanol, ketones, such as acetone, aldehydes, such as acetaldehyde and other organic oxygen-containing compounds containing fewer than 6 carbon atoms per compound. Another type of catalyst which may be utilized to effect the alkylation reaction comprises the so-called "acid-acting" catalysts such as the mineral acids, including, particularly, hydrogen fluoride, sulfuric acid, phosphoric acid and mixtures thereof and the acid-acting composites of certain metallic oxides such as the silica-alumina, silica-zirconia and alumina-chromia composites.

The alkylation stage of the present process whereby the thiophene reactant is condensed with the alkylating agent is effected in the presence of the hereinabove specified catalysts at a temperature of from about -20° to about 175° C., preferably at temperatures within the range of from about 20° to about 120° C., and at a pres-

sure sufficient to maintain the reactants and catalyst in substantially liquid phase during the reaction. It is generally preferred in the present process when the more desirable mono-alkylated thiophene compounds are to be formed and when high conversions per pass are desirable that the reaction mixture contain a molar excess of the nuclearly substitutable thiophene reactant to be alkylated over the alkylating agent. An excess of the thiophene reactant also reduces the tendency of the reaction mixture to undergo foreign reactions, such as the polymerization or depolymerization of the alkylating agent (especially when an olefin is utilized as alkylating agent) or the decomposition or degradation of the thiophene reactant. Generally, from about 2 to about 20 molecular proportions of thiophene or a substitutable thiophene derivative to one molecular proportion of the alkylating agent provides a suitable molecular ratio of the reactants to obtain mono-alkylation and to obviate the undesirable results of having a corresponding lower ratio in the alkylation reaction. The unconverted reactants may be recovered and recycled for further use in the process.

The alkylation reaction may be effected either in a batch or continuous type of operation. In a typical batch type of treatment, the reactants comprising the nuclearly substituted thiophene compound and the alkylating agent are added to a stirred pressure vessel containing a predetermined quantity of the catalyst, followed by heating or cooling the mixture to the optimum alkylation temperature. The temperature is maintained at the optimum value and the pressure increased to provide liquid phase until the reaction mixture has attained substantial equilibrium. Following the completion of the reaction, the catalyst-containing phase, usually insoluble in the reactants present in the alkylation reactor, is separated from the mixture by the addition of water to the mixture (where the catalyst is soluble in the thiophene compounds) or by allowing the catalyst phase to settle and separate from the organic phase (when the catalyst is insoluble therein). The excess of thiophene reactant and the thiophene products of reaction are then washed to remove dissolved catalyst and/or promoter and the organic layer is dried and separated into fractions comprising the desirable products, for example by fractional distillation. The alkyl thiophenes may be reduced in boiling point, thereby minimizing the possibility of decomposition of the thiophenes during fractionation by conducting the distillation at a reduced pressure. The desired thiophene alkylates for conversion into detergents are removed as specific boiling fractions from the fractionating still and thereafter transferred to the sulfonation reactor for conversion to the corresponding sulfonic acids comprising the intermediates in the formation of the present detergent.

To effect sulfonation of the alkyl thiophene compound produced by the above alkylation reaction, the alkylate is contacted with a suitable sulfonating agent which may include sulfuric acid, usually of relatively dilute strength, below about 100% sulfuric acid and generally above about 75% acid, a halosulfonic acid such as fluoro- or chlorosulfonic acid, or anhydrous sulfur trioxide, preferably dissolved in a suitable solvent, such as sulfur dioxide, a paraffinic hydrocarbon or a halogenated hydrocarbon. The reaction is usually conducted at temperatures in

the neighborhood of room temperature, from about -10° to about 50° C. and preferably at temperatures of from about 0° to about 20° C. In order to prevent side reactions of the alkyl thiophene reactant during the sulfonation reaction, such as decomposition and/or oxidation thereof, the thiophene alkylate is dissolved in a suitable inert diluent such as a paraffinic hydrocarbon which is liquid at the sulfonation reaction temperature. Suitable inert diluents include such hydrocarbons as pentane, one or a mixture of the hexanes, heptanes, etc., such as petroleum ether and commercial hydrocarbon solvents such as "Skelly-solve C." Other inert diluents include halogenated hydrocarbons, such as carbon tetrachloride and the fluorocarbons, such as per-fluorobutane, an alcohol, such as methanol or ethanol, or an aromatic hydrocarbon such as benzene. The proportion of thiophene alkylate to diluent charged to the sulfonation reactor is usually maintained at from about 2 to about 10 volume proportions.

Following the sulfonation reaction, which is usually complete after a period of from about $\frac{1}{2}$ to 1 hour, the alkyl thiophene sulfonic acid may be separated from the sulfonating agent, diluent and other components of the reaction mixture and thereafter converted to the corresponding sulfonate salt by neutralizing the separated sulfonic acid with a suitable base, such as an aqueous solution of an alkali metal hydroxide. Alternatively the entire sulfonation reaction mixture, including the sulfonating reagent, may be neutralized, the mixture evaporated to dryness and the resultant dried product utilized as a detergent. If desired the alkyl thiophene sulfonate may be extracted from the inorganic sulfate salts with a suitable solvent, such as ethanol and the detergent recovered from the ethanol by evaporation of the solvent. When the entire mixture is neutralized, thus forming sulfate salts of the neutralizing agent, the resultant mixture of sulfonate and sulfate salts is preferably retained as such, since the sulfate salts of the neutralizing agent comprise valuable "builders" for the detergent. It is usually preferred in this type of operation, however, to separate a major proportion of the alkyl thiophene sulfonic acid from the sulfonation reaction mixture prior to neutralization because in many instances the neutralizing agent is more costly than the resulting sulfate salt of the neutralizing agent. It is generally more economical to introduce the builder salt into the detergent composition after the formation of the alkyl thiophene sulfonate and thus obviate the more costly procedure of neutralizing the entire sulfonation reaction mixture. In order to cause at least partial separation of the alkyl thiophene sulfonic acid from the sulfonation reaction mixture, it has been found that the sulfonic acid separates as a distinct, separate phase when a small amount of water is added to the reaction mixture and the diluted mixture cooled to cause the stratification of the sulfonic acid from the dilute sulfonating agent. Usually water in amounts ranging from about 1% to about 15% of the total sulfonating agent in the mixture is added to the sulfonation reaction mixture to effect the desired separation of the sulfonic acid. The insoluble sulfonic acid layer which separates by stratification from the diluted aqueous sulfonating agent is thereafter separated and reacted with the desired neutralizing agent.

The bases which in the form of their aqueous

solutions are utilizable as neutralizing agents of the sulfonic acid and which supply the cation portion of the alkyl thiophene sulfonate salts may be selected from the alkali metal hydroxides, such as lithium, sodium and potassium hydroxides, ammonia, suitable amino compounds, such as the primary, secondary and tertiary alkyl amines, and the primary, secondary and tertiary alkanol amines. Of the alkali metal hydroxides, sodium hydroxide in aqueous solutions having concentrations up to about 20% is preferred over the other more expensive alkali hydroxides except when detergents for the preparation of shaving or shampoo formulations are desired, in which case potassium hydroxide, ammonium hydroxide or an amine may be a more suitable neutralizing agent. The preferred amines and alkanol amines for use as neutralizing agents comprise those members whose sulfonate salts are readily soluble in aqueous solutions so that the resulting sulfonates may be utilized for purposes in which detergents are commonly employed. The amines of this type comprise, in general, the short chain aliphatic amines such as methyl, ethyl or propyl amines or such alkanol amines as ethanol or diethanol amines. In thus specifying bases utilizable as so-called "neutralizing" agent, it is not intended to infer that the sulfonic acid is necessarily made neutral, such that the aqueous solution thereof has a pH of 7. Rather, it is intended that the sulfonic acid be made substantially neutral; to the point of its optimum detergency.

The aqueous mixture formed by neutralizing the alkyl thiophene sulfonic acids which contains the desired neutralized salts thereof may be directly dried to form the final detergent product, or if desired, the solution may be composited with a suitable builder salt and then subsequently dried. Suitable builder salts, which when composited with the alkyl thiophene sulfonate detergent or utilized therewith in an aqueous solution of the detergent comprise one or a mixture of two or more salts selected from the group consisting of the water soluble alkali metal, ammonium, amine or alkanolamine salts such as the chlorides, phosphates, dihydrogen phosphates, sulfites, silicates, borates and thiosulfites thereof. The alkali metal sulfonates, chlorides, and silicates are preferred as builder salts and of these, sodium sulfate, sodium silicate and sodium chloride, are especially suitable for compositing with the detergent component. When incorporated into a detergent composition, the builder salt is added in sufficient amounts to comprise from 0 to about 80% by weight of the final detergent composition, preferably from about 35 to about 65% thereof. It is to be emphasized however, that the detergency activity of the alkyl thiophene sulfonate detergent is not wholly dependent upon the effect of the builder salt, but may be added to the detergent in the indicated amount to increase the efficiency of the detergent.

The builder salt is normally added to the aqueous solution or slurry of the alkyl thiophene sulfonate obtained upon neutralization of the preceding sulfonic acid and in accordance with customary procedure, resulting in maximum economy, the resulting aqueous slurry or solution of the components dried by evaporation of the water therefrom. The product is a composite of the individual components containing the same in intimate and homogeneous admixture such that both components dissolve substantially simultaneously when the composition is added to water. If desired, the aqueous slurry or solu-

tion may be spray dried to form spherically shaped particles of the composition which are characterized as being rapidly dissolvable in water and which contain a minimal quantity of detergent fines. Such procedures are known generally in the art and no necessity is seen for a detailed description of such procedures here.

The following example is introduced for the purpose of illustrating the method herein specified for the production of alkyl thiophene sulfonate detergents, although said example is not to be construed as limiting the generally broad scope of the invention in accordance thereto.

In a 5 liter flask immersed in a water bath maintained at 50° C. and equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser, was placed 300 ml. of a boron fluoride-water complex of approximate composition $\text{BF}_3 \cdot 2\text{H}_2\text{O}$, a mixture of 840 grams (10 mols) of thiophene and 840 grams (5 mols) of propylene tetramer of boiling point (760 mm.) 190–210° C. was added (with stirring) over a three hour period. The upper layer (product) was separated from the lower (catalyst layer), washed, dried, and distilled in vacuo. Over 50% of the material boiling above thiophene boiled (corrected to 760 mm. pressure) in the range 250–350° C. and corresponded in composition mainly to dodecylthiophene.

50 grams of the above prepared dodecylthiophene was dissolved in 500 ml. of pentane and added, slowly, with stirring to 150 ml. of 96% sulfuric acid, maintaining the temperature, meanwhile at or near 0° C. The sulfonated thiophene was formed in the lower layer which separated after the stirring was discontinued. The lower layer was carefully neutralized with N/10 sodium hydroxide. The exactly neutral (or very slightly basic) resulting solution was carefully

concentrated by removing water on a steam bath. The dry pulverized product contained considerable sodium sulfate, and was directly useable as a detergent.

I claim as my invention:

1. A thiophene sulfonate having attached to the thiophene nucleus an alkyl group containing from 9 to 18 carbon atoms.

2. A dodecylthiophene sulfonate.

3. The sodium salt of a dodecylthiophene sulfonic acid.

CARL B. LINN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,996,334	Hessle	Apr. 2, 1935
2,239,974	Reed	Apr. 29, 1941
2,336,916	Arnold et al.	Dec. 14, 1943
2,422,926	Reeves	June 24, 1947
2,469,378	Flett	May 10, 1949
2,469,823	Hansford	May 10, 1949

OTHER REFERENCES

Bernthsen and Sudborough: Organic Chemistry, p. 549, Van Nostrand, N. Y. (1925), 1922 ed.

Whitmore: Organic Chemistry, pp. 884, 893, Van Nostrand, N. Y., 1937.

Richter: Organic Chemistry, pp. 649, 650, Wiley, N. Y., 1938.

Powers: Advancing Fronts in Chemistry, vol. II, p. 33, Reinhold Pub. Co., N. Y., 1946.

Williams: Detoxication Mechanisms, p. 194, Wiley, N. Y., 1947.

Steinkopf: Die Chemie des Thiophens, p. 21, Edwards lithoprint of 1941 publication.