April 12, 1949. M. HUNT ET AL 2,467,130

ALKYL SUBSTITUTED AROMATIC SULFONATES

Filed Oct. 15, 1947 2 Sheets-Sheet 1

FIG. I.

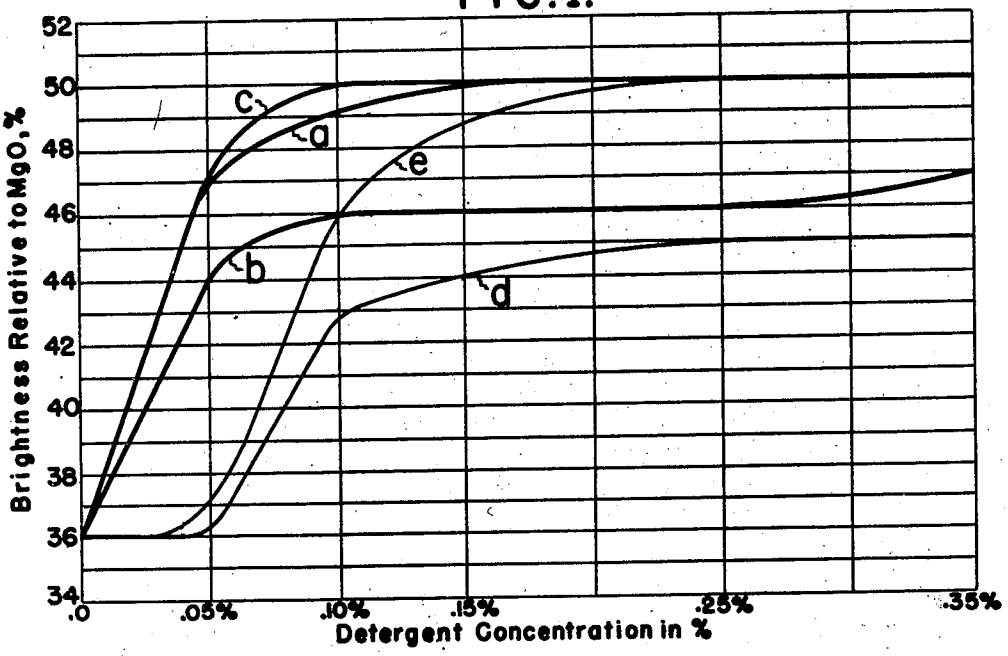
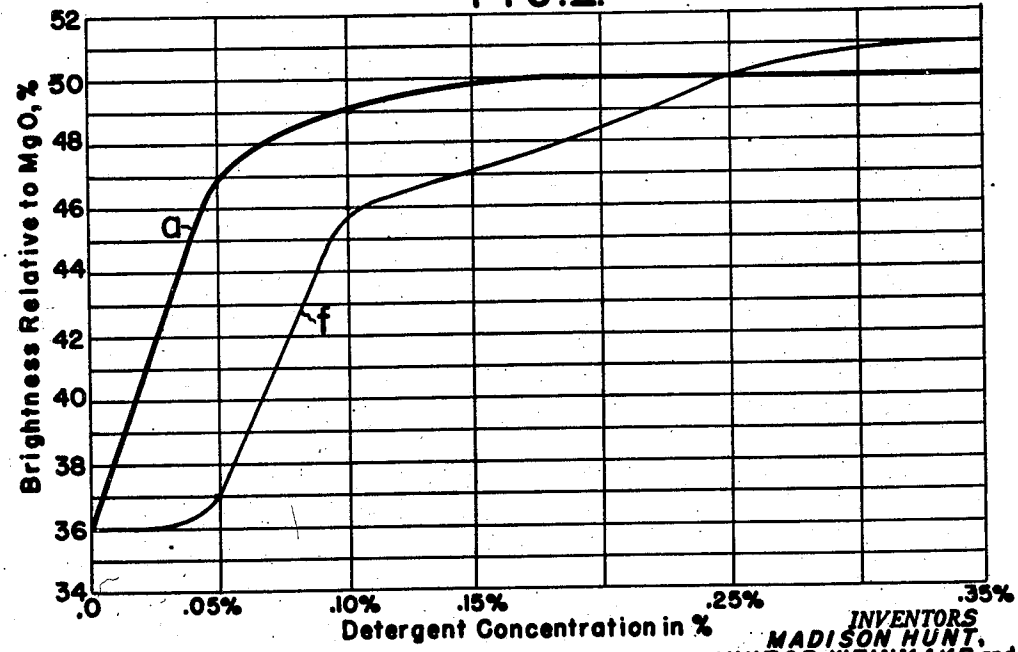


FIG. II.



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FIG. III.

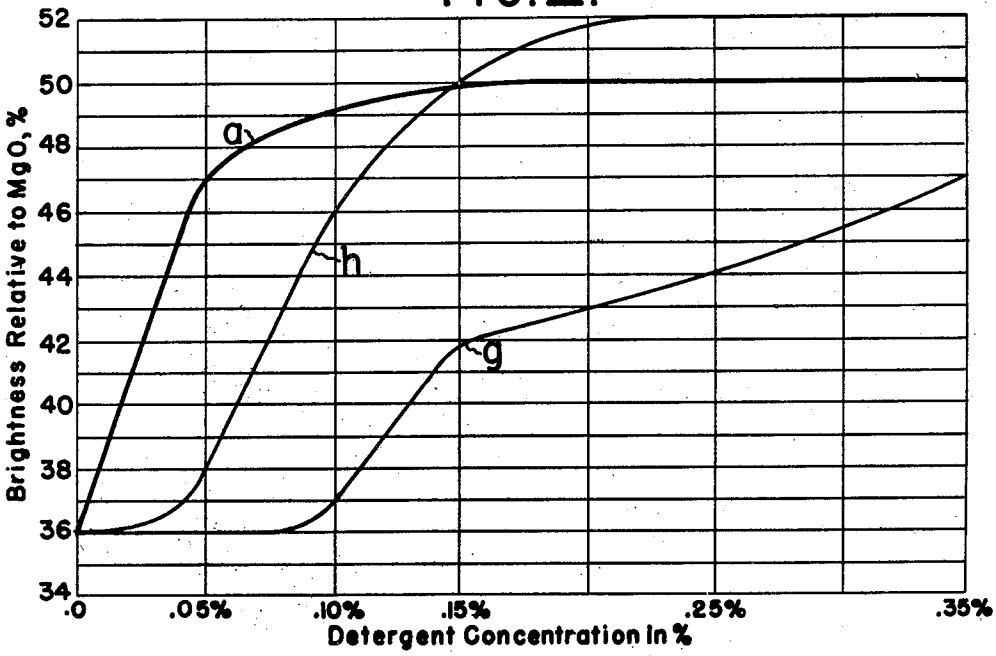
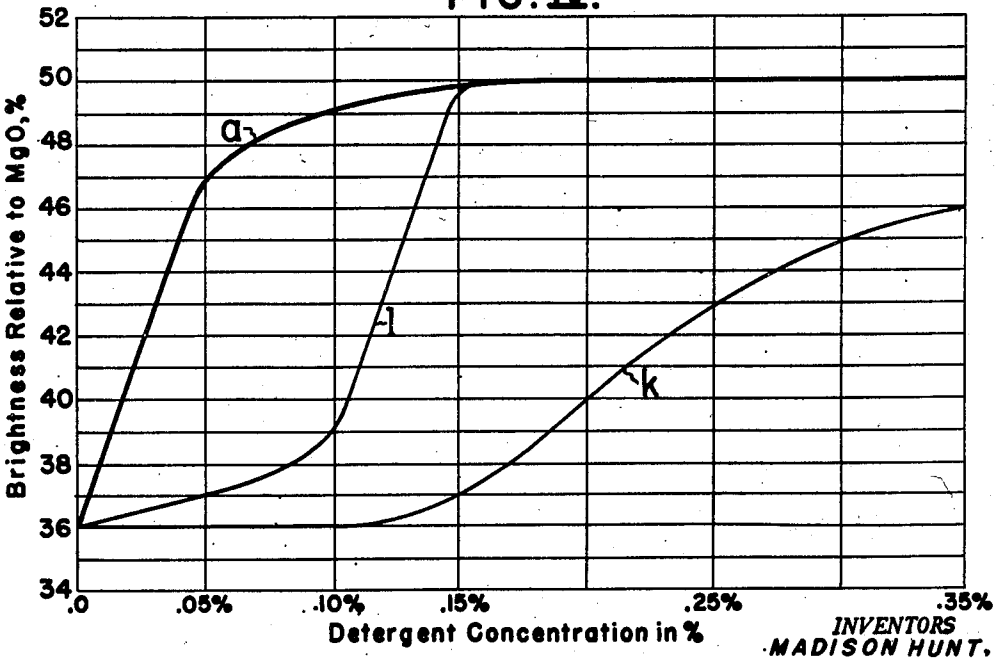


FIG. IV.



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UNITED STATES PATENT OFFICE

2,467,130

ALKYL SUBSTITUTED AROMATIC SULFONATES

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Application October 15, 1947, Serial No. 780,096

6 Claims. (Cl. 260—505)

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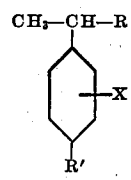
This invention deals with a group of alkylaromatic sulfonic acids and their salts useful as surface active agents, particularly as detergents and wetting agents.

It is an object of this invention to provide new detergent compounds of superior detergent power in hard water.

The use of alkylated aromatic sulfonic acids as detergents as a general proposition is well known. Both sulfonated naphthalene and benzene derivatives have been indicated in the art, and the length of the alkyl chain has been varied from as low as 3 carbon atoms to as high as 20 carbon atoms, both straight-chain and branched-chain radicals being often employed.

We have now found that the limited group of compounds having the particular structure defined hereinbelow possesses outstanding qualities as detergents, being superior to hitherto described compounds as regards detergent power at low concentrations in hard water.

The novel compounds embraced in this invention are characterized by possessing a sulfonated benzene ring which is attached to the 2-carbon atom of a normal alkane having from 10 to 13 carbon atoms; in addition, the benzene ring is characterized by possessing a methyl or ethyl radical in position para to the aforementioned long-chain alkyl radical. Altogether then, the compounds of this invention are defined by the formula



wherein R is a straight-chain, saturated aliphatic hydrocarbon radical of 8 to 11 carbon atoms, R' designates a methyl or ethyl radical, while X represents the sulfonic acid radical or a salt thereof.

This invention embraces the above compounds in free acid form as well as in the form of water-soluble salts thereof, as obtained for instance by neutralizing the free acid with inorganic or organic bases. For the purpose of this invention, the term "water-soluble" shall be construed as meaning that the compound concerned is soluble

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in water to an extent of at least 0.2% by weight.

The products of this invention are prepared by sulfonating the corresponding hydrocarbon with oleum and, if desired, neutralizing the sulfonic acid thus formed with an alkali-metal hydroxide, an alkaline-earth hydroxide, or any other alkaline agents such as primary, secondary or tertiary amines or quaternary nitrogenous bases. The alkylaromatic compounds themselves may be prepared by any suitable synthesis, such as the Friedel-Crafts reaction or reactions based on a Grignard synthesis. These methods of preparation are illustrated in the following examples, which however are given merely for illustrative purposes, without any intent to limit the invention thereby.

The annexed drawing represents graphically the data obtained in our tests on the novel compounds and reported in the tables hereinbelow.

EXAMPLE 1.—2-(p-METHYLPHENYL)-DODECANE

A. *Preparation of the hydrocarbon*

To a mixture of 21.5 parts of anhydrous hydrogen fluoride and 40 parts of toluene, maintained at a temperature of 0–5° C. in a copper or nickel vessel, 16.8 parts of dodecene-1 are added slowly with agitation so as to maintain the mass within said temperature interval throughout. When addition has been completed, the mixture is stirred for eighteen hours at 0–10° C. The reaction mixture is then poured slowly into 550 parts of water, and the upper organic layer is separated and washed, first with water and then with 5% sodium carbonate solution. After removal of the excess toluene by distillation, the product is distilled under vacuum. 22.4 parts of a product boiling at 130° C. at 2 mm. pressure are thus obtained. The product gives a refractive index of $n_D^{20}=1.4855$ and a density of

$$D_{20}^{20}=0.8497$$

B. *Sulfonation*

To 15 parts of the above product, 27 parts of 20% oleum are added slowly with cooling and agitation so as to hold the temperature at 20–30° C. After all of the oleum has been added, the temperature of the reaction mixture is raised to 45–50° C. and held at this temperature for one-half hour. The product is poured into 90 parts of

water, and 10 parts of alcohol are added in order to obtain a homogeneous solution. The mixture is neutralized to a pH of 7–8 with 20% sodium hydroxide solution. The mixture is drum-dried to yield 50 parts of a product containing about 40% active ingredient and 60% sodium sulfate. The active ingredient may be isolated in a pure state by extraction of the 40% product with hot alcohol.

Instead of sodium hydroxide in the above example the corresponding equivalent weight of any other hydroxide or base which leads to a water-soluble sulfonate may be used, for instance potassium hydroxide, calcium hydroxide, magnesium hydroxide, ammonia, monomethylamine, dimethylamine, trimethylamine, tetramethylammonium hydroxide, the corresponding ethyl amines, the various ethanolamines (mono-, di- and tri-), etc.

EXAMPLE 2.—PREPARATION AND SULFONATION OF 2-(P-METHYL-PHENYL)-DECANE

To a mixture of 50 parts of toluene and 15 parts of anhydrous hydrogen fluoride are added 10 parts of decene-1 at a temperature of 0–5° C. After addition is complete, the mixture is stirred at 0–10° C. for eighteen hours. The mixture is poured slowly into 300 parts of ice-water and the upper organic layer is separated. The product is washed with water and finally with 5% sodium carbonate solution. After removal of the excess toluene by distillation, the product is distilled in vacuum. The fraction boiling at 108° C. at 3 mm. is collected. A sample of this product gave a refractive index of $n_D^{20}=1.4871$ and a density of

$$D_{20}^{20}=0.8574$$

Analysis: Calculated for $C_{17}H_{28}$, C=87.8, H=12.2. Found, C=86.1, H=12.1.

The above product is sulfonated and optionally neutralized as described in Example 1. After drum-drying, a product of light cream color is obtained. This material is soluble in water to give a foaming solution.

EXAMPLE 3.—PREPARATION AND SULFONATION OF 2-(P-ETHYL-PHENYL)-DODECANE—GRIGNARD SYNTHESIS

To a suspension of 15 parts of magnesium in 450 parts of anhydrous ether 132 parts of n-decyl bromide are added dropwise, with stirring, at reflux temperature. The rate of addition is adjusted so that the heat of reaction maintains the refluxing of the ether. After addition of the bromide is complete, the mixture is refluxed for one hour. A solution of 74 parts of the p-ethylacetophenone (prepared according to A. Klages, Ber., 32, 1558 (1899)) in 150 parts of anhydrous ether is added over a period of one hour, and the mixture is refluxed an additional half hour. The reaction mixture is poured into ice water and acidified with hydrochloric acid. The upper layer is separated, extracted with 5% sodium carbonate solution, and dried over anhydrous magnesium sulfate. After removal of the drying agent and the ether, the product is heated at 200° C. for 2 hours with 30 parts of sodium acid sulfate. Upon distillation, a product boiling at 166° C. (at 8 mm. pressure) is obtained, which is a mixture of 2-(p-ethylphenyl)-dodecene-1 and 2-(p-ethylphenyl)-dodecene-2.

The hydrogenation to a saturated hydrocarbon is carried out by dissolving 54 parts of the above product in 150 parts of glacial acetic acid, adding 0.1 part of platinum oxide catalyst ("Organic Synthesis," collected volume I, p. 452) and shaking the mixture at 20–30° C. and three atmospheres hydrogen pressure. Reduction is complete within one hour. The catalyst is removed by filtration and the acetic acid separated by distillation. The product is distilled and the material boiling at 165° C. at 9 mm. pressure is collected. The product has a refractive index of $n_D^{20}=1.4790$ and a density of

$$D_{20}^{20}=0.8501$$

Analysis calculated for $C_{20}H_{34}$, C=87.6, H=12.5. Found: C=87.79, H=13.33.

The above product is sulfonated and neutralized with NaOH as described in Example 1, to yield a detergent mixture containing approximately 40% active ingredient and 60% sodium sulfate.

EVALUATION OF THE PRODUCTS

The evaluation of the above products for wetting power has been carried out as described in the AATC (American Association of Textile Chemists and Colorists) Year Book for 1946, page 230. The wetting power is gauged by the concentration in grams of active ingredient per liter of solution necessary to wet in 25 seconds. In Table V below, this concentration is designated as the standard wetting concentration. For detergent evaluation, the method described by O. C. Bacon, American Dyestuff Reporter, vol. 34, pages P556–P561, has been used. The results are expressed in tabular form using the percent reflectance of light from the surface of the soiled fabric relative to the reflectance of magnesium oxide as a measure of "brightness." The detergent is tested at five different concentrations.

Using these methods, the products of this invention show outstanding detergency at the low detergent concentrations in hard water. This is a real advantage even though at high concentration, other closely related structures may have approximately equal activity. At the same time, the wetting speed of the products of this invention is sufficiently high for practical purposes, and a significant improvement is noted over the products in which the phenyl group is attached to the 1-position on the aliphatic chain.

The following table illustrates the superiority of the p-methylphenyl compounds over the corresponding unsubstituted phenyl compounds at low detergent concentrations in hard water. The numerical values represent the percent reflectance of the washed fabric relative to magnesium oxide as 100%. The water employed in these tests contained 360 parts per million of alkaline earth chlorides calculated as calcium carbonate.

TABLE I

Graph No.	Compound	Detergent Concentration in percent					
		0	0.05	0.10	0.15	0.25	0.35
(a)	Sodium sulfonate of 2-(p-methylphenyl)-dodecane	36	47	49	50	50	50
(b)	Sodium sulfonate of 2-(p-ethylphenyl)-undecane	36	44	46	46	46	47
(c)	Sodium sulfonate of 2-(p-ethylphenyl)-dodecane	36	47	50	50	50	50
(d)	Sodium sulfonate of 2-phenyldecane	36	36	43	44	45	45
(e)	Sodium sulfonate of 2-phenyldodecane	36	37	46	49	50	50

The above data are reproduced graphically in Figure I, wherein the individual curves have been designated respectively *a*, *b*, *c*, *d*, and *e* to correspond with the items in the above table. It will

be noted that curves *d* and *e* drop considerably below curves *a*, *b* and *c* in the region of low concentrations.

The effect of the para methyl group in enhancing detergency is not observed when methyl groups are introduced into positions other than the para position. This is shown in Table II.

TABLE II

Graph No.	Compound	Detergent Concentration in percent					
		0	0.05	0.10	0.15	0.25	0.35
(*a*)	Sodium sulfonate of 2-(p-methylphenyl)-dodecane	36	47	49	50	50	50
(*f*)	Sodium sulfonate of 2-(2,5-dimethylphenyl)-dodecane	36	37	46	47	50	51

The data in this table are reproduced graphically in Figure II, the curves being marked to correspond.

If one of the methyl groups in the 2,5-dimethylphenyl compound is moved into the para position as in the 2,4-dimethylphenyl derivative or the 3,4-dimethylphenyl derivative the enhanced detergency in hard water reappears.

The effect of branching the long aliphatic chain is to decrease the value of the compound as a detergent. This is shown in the following table:

TABLE III

Graph No.	Compound	Detergent Concentration in percent					
		0	0.05	0.10	0.15	0.25	0.35
(*a*)	Sodium sulfonate of 2-(p-methylphenyl)-dodecane	36	47	49	50	50	50
(*g*)	Sodium sulfonate of toluene alkylated with polymerized propylene (C_{12})	36	36	37	42	44	47
(*h*)	Sodium sulfonate of benzene alkylated with polymerized propylene (C_{12})	36	38	46	50	52	52

The graphs pertaining to this table are given in Figure III, the individual curves being marked to correspond.

The polymerized propylene (C_{12}), which gives a good detergent when alkylated onto benzene, is a mixture of highly branched twelve carbon chains. However, the product from polypropylene (C_{12}) and benzene is much inferior at low detergent concentrations in hard water to the products of this invention. The toluene derivative is a very poor detergent.

The introduction of groups larger than ethyl into the para position on the benzene ring does not give the enhancement of detergency noted with methyl or ethyl groups. This is illustrated in the following table:

TABLE IV

Graph No.	Compound	Detergent Concentration in percent					
		0	0.05	0.10	0.15	0.25	0.35
(*a*)	Sodium sulfonate of 2-(p-methylphenyl)-dodecane	36	47	49	50	50	50
(*k*)	Sodium sulfonate of 2-(p-isopropylphenyl)-dodecane	36	36	36	37	43	46
(*l*)	Sodium sulfonate of 2-(p-isopropylphenyl)-decane	36	37	39	50	50	50

For the corresponding curves, see Figure IV.

The location of the p-tolyl radical in the 2-position of the alkane is particularly advantageous, because these compounds are readily

available by alkylation of terminally unsaturated olefines. In addition, the wetting speed of compounds with the aryl group attached to the 2-position is much better than the corresponding 1-substituted compounds as shown in the following table:

TABLE V

Compound	Standard wetting concentration in g./l.
Sodium sulfonate of 2-(p-methylphenyl)-dodecane	0.9
Sodium sulfonate of 2-(p-methylphenyl)-decane	0.8
Sodium sulfonate of 2-(p-ethylphenyl)-dodecane	1.2
Sodium sulfonate of 1-(p-methylphenyl)-dodecane	over 1.5

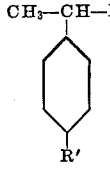
It will be understood that many variations are possible in the methods of synthesizing the novel compounds and in the choice of base for neutralizing the sulfonic acid group. Apart from the last-mentioned freedom of variation, however, the number of sulfonic acids falling within the scope of this invention is limited and is represented in fact by the following 8 compounds:

2-(p-methylphenyl)-decanesulfonic acid
2-(p-methylphenyl)-undecanesulfonic acid
2-(p-methylphenyl)-dodecanesulfonic acid
2-(p-methylphenyl)-tridecanesulfonic acid
2-(p-ethylphenyl)-decanesulfonic acid
2-(p-ethylphenyl)-undecanesulfonic acid
2-(p-ethylphenyl)-dodecanesulfonic acid
2-(p-ethylphenyl)-tridecanesulfonic acid

The products of this invention are useful as surface active agents, particularly as detergents and wetting agents. The products show unusually high detergency at low concentrations in hard water. It is expected that in actual practice, the concentrations employed will generally fall within the limits indicated in the above tables.

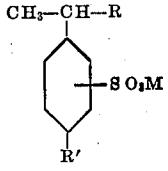
We claim as our invention:

1. As new compounds, the monosulfonic acids and water-soluble monosulfonic acid salts of the hydrocarbons included in the following formula



wherein R is a straight-chained, saturated, aliphatic hydrocarbon radical of not less than 8 and not more than 11 carbon atoms, while R' is an alkyl radical of less than three carbon atoms.

2. The dialkyl-benzene-sulfonates of the general formula



wherein M is an alkali-metal, R is a straight-chained alkyl radical of 8 to 11 carbon atoms, while R' is an alkyl radical of not over two carbon atoms.

3. The sodium sulfonate of 2-(p-methylphenyl)-dodecane.

4. The sodium sulfonate of 2-(p-methylphenyl)-decane.

5. The sodium sulfonate of 2-(p-ethylphenyl)-dodecane.

6. A detergent composition comprising as active ingredient a compound consisting of a normal alkane of not less than 10 and not more than 13 carbon atoms bearing in the 2-carbon atom a monosulfonated benzene radical which in turn bears in p-position an alkyl radical selected from the group consisting of methyl and ethyl.

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MARIO FRANCESCO SARTORI.

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