

UNITED STATES PATENT OFFICE

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SULPHONATED ETHERS

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It has been found that new sulphonated ethers containing at least one aralkyl radical are obtained if sulphonated hydroxy compounds are etherified by treatment with aralkylating agents containing at least 8 carbon atoms, or if hydroxy compounds are etherified by treatment with aralkylating agents containing at least 8 carbon atoms and the ethers obtained are thereupon sulphonated.

Among sulphonated hydroxy compounds both hydroxy-sulphonic acids as well as sulphuric acid esters of polyhydroxy compounds which contain at least one free hydroxy group are to be understood.

As hydroxy sulphonic acids, use may be made, for example, of those of the aliphatic series, such as hydroxyethane sulphonic acid, chlorohydroxypropane sulphonic acids, dihydroxypropane sulphonic acids, but preferably, however, of aromatic hydroxysulphonic acids, for instance hydroxy sulphonic acids containing at most two condensed benzene nuclei, that is to say hydroxy sulphonic acids of the benzene and naphthalene series such as mono-hydroxy and dihydroxy naphthalene sulphonic acids. Among these mention may be made of phenol-para-sulphonic acid, chlorophenol sulphonic acids, cresol sulphonic acids, thymol sulphonic acids, such as 3-hydroxy-1-methyl-4-isopropylbenzene sulphonic acid-(6), sulphonic acids of resorcinol, such as 1:3-dihydroxybenzene sulphonic acid-(4), sulphonic acids of mono- and polyhydroxynaphthalenes, such as 1-hydroxynaphthalene sulphonic acid-(4), 1-hydroxy-naphthalene sulphonic acid-(5), 2-hydroxynaphthalene sulphonic acid-(6), 2-hydroxynaphthalene disulphonic acid-(3:6), 1:3-dihydroxy-naphthalene sulphonic acid-(5), 1:3-dihydroxy-naphthalene sulphonic acid-(6), 2:8-dihydroxynaphthalene sulphonic acid-(6), 2:3-dihydroxy-naphthalene sulphonic acid-(6), 1:8-dihydroxynaphthalene sulphonic acid-(4), 1:8-dihydroxynaphthalene disulphonic acid-(3:6), 2-hydroxynaphthalene carboxylic acid-(3)-sulphonic acid-(6); also hydroxysulphonic acids of tetrahydronaphthalene, such as ar-tetrahydro- α -naphthol-4-sulphonic acid; furthermore hydroxysulphonic acids of diphenyl, anthracene, phenanthrene, and acenaphthene, etc. Apart from the halogen atoms and carboxyl groups already mentioned, the hydroxysulphonic acids can also contain other substituents, for example, amino groups, substituted amino groups (such as acylated amino groups), methoxy groups, etc.

Cycloaliphatic hydroxysulphonic acids such as

hydroxycyclohexane sulphonic acids also come into consideration.

Among the sulphuric acid esters of polyhydroxy compounds which also come into consideration as parent materials, mention may be made of the monosulphuric acid esters of glycol and glycerine.

Chloromethyl compounds of aromatic or partially hydrogenated aromatic compounds are particularly suitable for use as aralkylating agents containing at least 8 carbon atoms. Examples of such substances are: chloromethyl toluene, chloromethyl xylene, chloromethyl cumene, 2-chloromethyl cymene, 1-chloromethyl naphthalene, chloromethyl-tetrahydronaphthalenes, such as ar-2-chloromethyl-tetrahydronaphthalene, chloromethyl-cyclohexyl benzene (prepared, for example, by treating the addition product of benzene and cyclohexene with formaldehyde, aqueous hydrochloric acid, and hydrogen chloride gas at 60-70° C.), chloromethyl compounds of higher condensed aromatic ring systems and of their partially hydrogenated derivatives, for example, chloromethylantracene, chloromethyl-octahydroanthracene, chloromethyl-octahydrophenanthrene.

The chloromethyl derivatives of aromatic and partially hydrogenated aromatic hydrocarbons which are not yet described in the literature can be prepared directly by analogous processes, for example, by introducing hydrogen chloride gas into a mixture—warmed to about 60-70° C.—of the hydrocarbon, concentrated formaldehyde solution, and concentrated aqueous hydrochloric acid, if desired together with an addition of zinc chloride.

As aralkylating agents, use may also be made of chloromethyl derivatives of hydroxyaryl compounds, for example, the chloromethyl compound of the phenol-like addition product of phenol and dipentene, also chloromethyl compounds of ethers containing aryl radicals, for example, the chloromethyl compound of the ether obtained by condensation of dipentene with β -naphthol. These chloromethyl compounds can be obtained from the hydroxyaryl compounds—sometimes described, sometimes to be had directly by analogous processes—and their ethers in the manner already described for the chloromethyl derivatives of hydrocarbons.

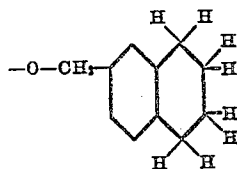
The reaction of the sulphonated hydroxy compounds, for example, of the hydroxyaryl sulphonic acids, with the aralkylating agents takes place preferably at raised temperature, if desired under addition of acid binding agents, such as sodium hydroxide, sodium carbonate, or calcium

carbonate. For example, it is possible to react the aralkyl chlorides with aqueous solutions of the neutralized hydroxyaryl sulphonic acids at 60-70° C., the reaction of the solution being kept alkaline by addition of sodium hydroxide.

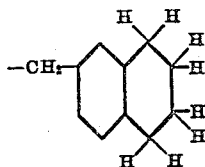
One method of carrying out the present process consists of reacting the aralkylating agents containing at least 8 carbon atoms with the unsulphonated hydroxy compounds, instead of with the corresponding sulphonated hydroxy compounds—this can take place in the manner already described for the hydroxysulphonic acids—and then sulphonating the ethers thus obtained by treatment with sulphonating agents, such as concentrated sulphuric acid, chlorosulphonic acid, sulphuric acid containing sulphur trioxide.

The products of the present invention may be designated as sulphonated ethers containing at least one aralkyl radical with at least 8 carbon atoms bound to an ether oxygen atom, which products in the form of the alkali metal salts are solid to liquid substances soluble in water to form stable capillary active solutions. Other salts than the above mentioned alkali metal salts including ammonium salts, such as amine salts, for instance alkylolamine salts may also be obtained according to the present invention.

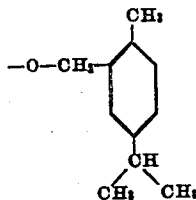
The ether sulphonic acids obtained in the reaction of aromatic hydroxy sulphonic acids are sulphonic acids in which at least one nuclear hydrogen atom is substituted by a radical of the formula $-O-R$, wherein R stands for an aralkyl radical with at least 8 carbon atoms. The reaction with ar-2-chloromethyl-tetrahydronaphthalene leads to sulphonic acids in which at least one nuclear hydrogen atom is substituted by at least one radical of the formula



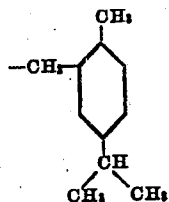
the radical



representing a tetrahydronaphthylmethyl radical. The corresponding reaction with 2-chloromethylcymene yields sulphonic acids which are substituted by at least one radical of the formula



the radical



representing a cymyl-methyl radical.

Thanks to their capillary activity, the products of the invention can be used as textile auxiliary products, for example, as wetting, dispersing, washing, softening, levelling, or foaming agents.

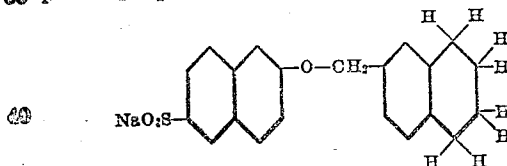
Products of the invention which have nuclear alkylated benzyl radicals, especially those having two such radicals—which may be introduced by means of chloromethyl cymene—are excellent wetting agents. These cymyl-methyl derivatives possess a much higher wetting capacity than corresponding products which contain naphthylmethyl or tetrahydronaphthylmethyl radicals instead of cymylmethyl radicals. Products containing tetrahydronaphthylmethyl radicals are noteworthy for their good washing action.

The products of the present invention can be used alone or in combination with other substances which are commonly used in conjunction with textile auxiliary products, for example, inorganic salts.

The following examples illustrate the invention, the parts being by weight:

Example 1

28 parts of a technical sodium salt of 2-hydroxynaphthalene-6-sulphonic acid, containing a calculated quantity of 22.5 parts of the acid, are dissolved in 100 parts of caustic soda of 4 per cent. strength, and 17.5 parts of ar-2-chloromethyltetrahydronaphthalene are added whilst stirring at 60-65° C. After about 30 minutes a clear solution is formed which has a neutral reaction. The solution is evaporated to dryness under reduced pressure on the water bath and 47 parts of a pale yellow residue of the formula



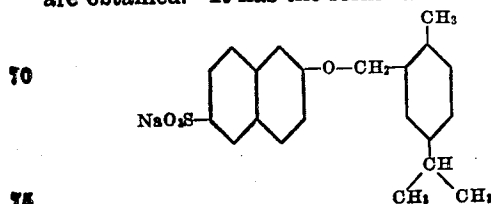
are obtained, which is readily pulverizable.

The produce yields a clear solution in water and is not precipitated therefrom by acidifying with mineral acid. Its solutions foam strongly and possess good washing powers.

Instead of the sodium salt of 2:6-hydroxynaphthalene-sulphonic acid the corresponding ammonium salt or an alkylolamine salt may be used. Moreover, these salts may be replaced by the sodium salt of the β -hydroxyethane sulphonic acid or of the acid sulphuric acid ester of ethylene glycol.

Example 2

28 parts of a technical sodium salt of 2-hydroxynaphthalene-6-sulphonic acid with a calculated content of 22.5 parts of the acid are dissolved in 100 parts of caustic soda of 4 per cent. strength and 17.5 parts of 2-chloromethylcymene are added at 75-80° C. whilst stirring well. After about 1½ hours an almost clear solution is obtained which has a neutral reaction. This reaction solution is evaporated to dryness, when 45 parts of a pale yellow, easily pulverized residue are obtained. It has the formula

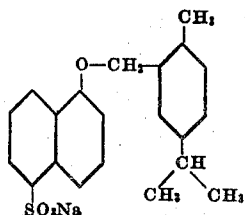


The product yields a clear solution in water and is not precipitated therefrom when acidified with mineral acid. The aqueous solution foams strongly and possesses good wetting and washing powers.

Example 3

30.3 parts of the technical sodium salt of 1-hydroxynaphthalene-5-sulphonic acid (73.9 per cent. sulphonic acid content) are dissolved in 80 parts of water and the solution is neutralized with caustic soda. 13.5 parts of a solution of caustic soda of 30 per cent. strength are then added; the solution is heated to 65–70° C. and, whilst stirring, 18 parts of 2-chloromethylcymene are introduced. After stirring for 1½ hours a sample of the reaction mixture should give a clear solution with water. It is now neutralized exactly and evaporated to dryness.

The sodium salt of the cymylmethyl ether of 1-hydroxynaphthalene-5-sulphonic acid which is obtained and which has the formula

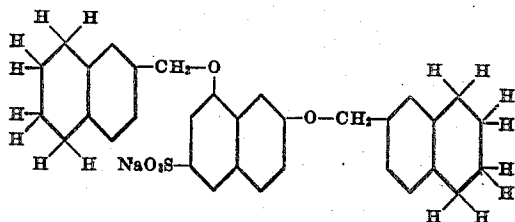


is a pale yellow powder, readily soluble in water. Its aqueous solutions possess pronounced washing, foaming and wetting properties.

Example 4

32.5 parts of a technical sodium salt of 2:8-dihydroxynaphthalene-6-sulphonic acid with a calculated content of 24 parts of the acid are dissolved in 100 parts of water and are made neutral to Congo Red paper with dilute caustic soda. 26.5 parts of caustic soda of 30 per cent. strength and 36 parts of ar-2-chloromethyltetrahydronaphthalene are added and the mixture is strongly stirred at 60–65° C. Very soon a reddish, putty-like mass begins to separate and, after 1½ hours, the reaction mixture is no longer alkaline to phenolphthalein. A sample of the mass dissolves in water with only a faint turbidity. The filtered aqueous solution of the reaction mass is then evaporated to dryness.

The new product of the formula



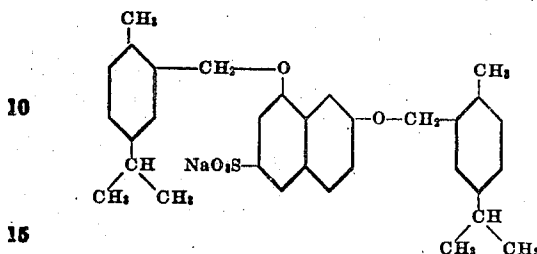
is readily soluble in hot water and is not precipitated from such a solution by mineral acid. The aqueous solution foams strongly.

Example 5

32.5 parts of a technical sodium salt of 2:8-dihydroxynaphthalene-6-sulphonic acid (73.8 per cent. of sulphonic acid) are dissolved in 100 parts of water and the solution is neutralized with caustic soda. 27 parts of a solution of caustic soda of 30 per cent. strength are then added; the solution is heated to 65–70° C. and, whilst stirring, 36 parts of 2-chloromethylcymene are added. After stirring for 10 hours the sodium salt of the di-

cymylmethyl ether of 2:8-dihydroxynaphthalene-6-sulphonic acid separates as a semisolid mass which becomes solid on cooling and is then filtered off.

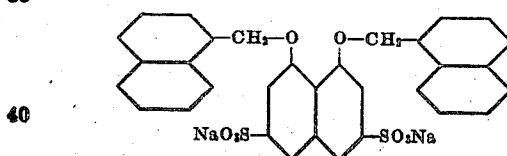
The new product thus obtained of the formula



dissolves in water to yield solutions that foam strongly and are pronouncedly capillary active.

Example 6

46 parts of a technical sodium salt of 1:8-dihydroxy-naphthalene-3:6-disulphonic acid with a calculated acid content of 32 parts are suspended in 100 parts of water and are neutralized to Congo Red paper by addition of dilute caustic soda solution. On adding 26.5 parts of caustic soda solution of 30 per cent. strength a brown solution is formed which is stirred with 36 parts of 1-chloromethyl-naphthalene at 60–65° C. After 1¼ hours the reaction mixture is neutral to Brilliant Yellow paper and a slimy mass separates out. A sample of the latter gives a clear solution in water. After evaporation and drying of the reaction mixture, 80 parts of an easily pulverized residue of the formula



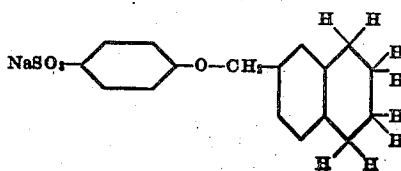
are obtained.

The product gives a clear solution in water and is not precipitated therefrom by acidification with mineral acid. The aqueous solution foams strongly and possesses good washing power.

In a similar manner 2-chloromethylcymene instead of 1-chloromethylnaphthalene may be condensed with the 1:8;3:6-dihydroxy-naphthalene disulphonic acid.

Example 7

19.6 parts of sodium para-phenolsulphonate are dissolved in 50 parts by volume of 2n-sodium hydroxide solution at 40–50° C. 18 parts of ar-2-chloromethyltetrahydronaphthalene are added and the mixture is stirred at 70–75° C. with an active stirrer. After a reaction period of 7 hours the alkaline reaction of the reaction mass has disappeared, and a sample of the mass gives a strongly foaming solution on shaking with water. To remove small quantities of by-products which are insoluble in water, the reaction solution is evaporated to dryness and the residue is extracted with ether, when the sodium salt of paratetrahydronaphthyl-methyl-hydroxy-benzene sulphonate of the formula



remains as an almost white powder which dissolves in water to yield a foaming solution and possesses pronounced washing action, especially in the presence of common salt.

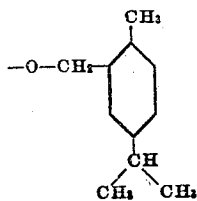
Example 2

For the washing of woollen yarn a bath is prepared which contains 0.3 to 0.5 gram of the product obtained in Example 1 per liter of water at 45° C., the ratio of goods to liquor being 1:20. The material is entered into the bath, turned for ½ hour and then rinsed. After this treatment the wool is excellently clean and can be dyed directly without trouble.

What we claim is:

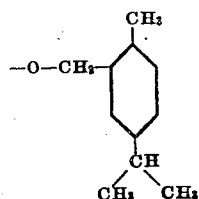
1. Aromatic sulphonic acids in which at least one nuclear hydrogen atom is substituted by a radical of the formula —O—R , wherein R stands for an alkylated benzyl radical, free from sulphonic acid groups, with at least 11 carbon atoms, which products in the form of the alkali metal salts are solid to liquid substances soluble in water to form stable capillary active solutions.

2. Sulphonic acids of the naphthalene series in which at least one nuclear hydrogen atom is substituted by the radical of the formula



which products in the form of the alkali metal salts are solid to liquid substances soluble in water to form stable capillary active solutions.

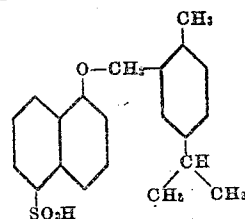
3. Sulphonic acids of the naphthalene series in which one nuclear hydrogen atom is substituted by the radical of the formula



which products in the form of the alkali metal

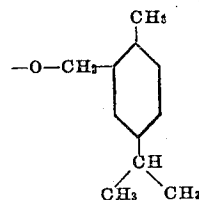
salts are solid to liquid substances soluble in water to form stable capillary active substances.

4. The sulphonic acid of the formula



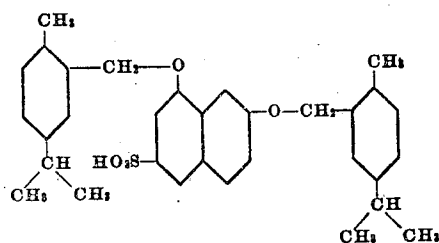
which product in the form of the sodium salt is a solid substance soluble in water to form stable capillary active solutions of a good washing power.

5. Sulphonic acids of the naphthalene series in which two nuclear hydrogen atoms are substituted by radicals of the formula



which products in the form of the alkali metal salts are solid to liquid substances soluble in water to form stable capillary active solutions.

6. The sulphonic acid of the formula



which product in the form of the sodium salt is a solid substance soluble in water to form stable capillary active solutions of a good washing power.

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