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SULPHO ACIDS AND PROCESS OF MANUFACTURE

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9 Claims. (Cl. 260—108)

This invention relates to new compositions of matter in the form of sulpho acids of aromatic compounds and to a process for producing the same. More particularly, the invention is concerned with the production of compounds of this general nature in which the aromatic nucleus has more than one ring and further in which one or more alkyl or cycloalkyl groups having more than five carbon atoms have been substituted. In addition, compounds according to this invention contain at least one sulpho group and are characterized by the fact that an alkyl residue and a fatty acid residue are bound with the aromatic nucleus.

The invention also contemplates the conversion of the sulpho acids into salts suitable for various commercial purposes as will more fully be described hereinafter. The salts obtained, as do the acids themselves, possess excellent wetting, foaming and dispersive or spreading powers, and they may therefore advantageously be used for a number of purposes, particularly in the textile, leather and similar industries. In addition, the salts or the acids are well adapted for use in carbonizing solutions employed in the textile industry, and thus assisting in the production of aqueous solutions of compounds of high molecular weight, such as dye-stuffs. The compounds of this invention are still further highly effective as agents tending to promote emulsification and suspension. In addition my improved compounds have a preservative effect upon materials treated, probably because of the presence of the fatty acid radical.

The compounds of this invention, moreover, may be employed as soaps or added to soaps, and further they may serve as water softeners and as fat splitting agents, in which latter capacity they possess much greater efficiency than the Twitchell reagent. In this connection it is pointed out that an especially effective washing action is secured when employing compounds embodying the higher aliphatic alcohols. Where the higher aliphatic alcohols employed have more than six carbon atoms, the improvement in washing effect is noticeable, although I have found it to be preferable to employ alcohols having in excess of eleven carbon atoms since this produces the best washing action.

Still further use for the compounds produced in accordance with this invention is involved in the mixture thereof with organic solvents such for example as cyclohexanol, tetrahydronaphthalene and other sulphonation products of fats or fatty alcohols, for instance the products mentioned in my prior Patent No. 1,980,342.

In general, it may be said that the compounds of this invention are produced by bringing together a polynuclear aromatic compound, a fatty acid, and an alkylating agent and by condensation and sulphonation of these ingredients in the manner described more fully hereinafter.

As the polynuclear aromatic compounds I may employ naphthalene, anthracene, tetrahydronaphthalene, octahydroanthracene, as well as hydrocarbons of this type in which alkyl, halo-, oxy- or amino-groups have been substituted. As examples of these may be mentioned methylnaphthalene, benzylnaphthalene, cyclohexylnaphthalene, chloronaphthalene, naphthols, tetralols and naphthylamines.

The fatty acid employed is preferably chosen from the group represented by the class comprising lauric, myristic, palmitic, stearic, oleic, elaeosteric, and ricinoleic acids. These acids may be incorporated directly in the mixture or by employing compounds containing the acids. Esters, such as fats and oils, may be mentioned as examples of such compounds. More specifically, the fatty acid glycerin esters, oleic acid butyl ester, and lauric acid isopropyl ester, may be employed. Still further the anhydrides or halides of these acids may be used.

As mentioned above, the compounds of this invention also include in the molecule an alkyl or cyclo-alkyl group, preferably one having more than five carbon atoms. For this purpose such condensable alcohols as hexyl, octyl, decyl, particularly dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl and chloroctadecyl alcohols may advantageously be employed. It is also possible and sometimes desirable to use the sulphuric and phosphoric esters of these alcohols, as well as their phosphorchloride esters. Supplementing the alcohols mentioned, it is sometimes desirable to bring into reaction alcohols, having a low molecular weight, i. e., those having fewer than six carbon atoms to the molecule. Still further, aromatic and aliphatic-aromatic halo- or oxy-compounds may be used along with the alkyls or cycloalkyls mentioned above. For example, aralkyl compounds like benzyl alcohol, cresol, xylyl chloride, and benzyl chloride, as well as aromatic compounds like phenol, may be employed.

According to the invention, sulphonation and condensation of the substances mentioned may take place simultaneously or successively. If it is desired to perform condensation before sulphona-

tion, condensing agents such as phosphorous pentoxide, phosphorus oxychloride, thionyl chloride, zinc chloride and the like, may be used. In proceeding in this manner suitable diluents such as carbon tetrachloride, may be employed.

Sulphonation may, of course, be performed before condensation by sulphonating one or several of the compounds before bringing them together, in which event other agents promoting condensation may be employed, if necessary, when all of the ingredients to be used are brought together. As sulphonating agents I may mention the following: sulphoric acid, fuming sulphuric acid, sulphur trioxide, sulphuryl chloride or chlorosulphuric acid. As with condensation, it may be desirable to use the sulphonating agent in dilute form, in which case acetic anhydride, or a chlorinated carbon, such as trichlorethylene may be utilized advantageously.

I prefer to use the sulphonating agents mentioned above because, in addition to sulphonation, they also tend to promote condensation. Accordingly, where sulphonation and condensation can be performed simultaneously, it is often possible to dispense with the condensing agents and use the sulphonating agents in effecting both reactions.

In carrying out the process of my invention, the materials and agents are brought totgether or mixed. This may be facilitated by melting, by dissolving one in another, or by mechanical agitation. The temperatures should be above 40° C. and preferably between 40° C. and 60° C., with variations according to the materials used, etc.

It may also be desirable to add one ingredient to another gradually, as is noted in some of the following examples.

After the washing of the reaction product by aid of a mixture of ice and sodium chloride or sodium sulphate, the mass separates into layers, and the sulpho-acid is drawn off. The sulpho-acids may be further treated, if desired, by converting them into salts. The alkali salts, particularly sodium and potassium salts, are especially convenient for this purpose, but other salts may be produced, such as ammonium and amine salts of aliphatic and aromatic primary, secondary and tertiary bases such as methylamine, tetramethylammoniumhydroxide, aniline, pyridine, ethanol amine, hexylamine, cyclohexylamine, hydrogenated diphenylamine and the like.

Among the compounds to be condensed, those with double unions in the molecule occupy a special position since condensation with them is more easily effected so that the amount or number of condensing agents required is reduced.

It is evident that by selection of the components brought into reaction, one may obtain a wide variety of preparations possessing the desirable properties mentioned heretofore. Similarly, the proportions of the reacting masses and the temperatures employed may be varied with proportionate alterations in the characteristics of the end products. In the following examples, a few of the possible reaction combinations are described. It is to be understood that my invention is not limited to the specific instances given below.

Example 1

24 parts by weight hexadecyl alcohol are fused at 52° C. with 12.8 parts by weight naphthalene and sulphonated and condensed by 70 parts by weight of a sulphuric acid having a content of 25% sulphur trioxide. Then 15 parts by weight castor oil are added, whereupon condensation is effected at 50° C. by gradually adding a further 50 parts by weight of the sulphuric acid mentioned containing sulphur trioxide. After about 12 hours the sulphonate will be water soluble. The compound is washed with saturated Glauber's salt solution and neutralized with soda lye, at reduced temperature, if necessary. The product obtained is clearly soluble in water, practically without turbidity, and is resistant to mineral acids and magnesium sulphate. This compound is particularly suitable as a fat splitting agent.

Example 2

6 parts by weight hexadecanyl sulphuric acid are fused with 13 parts by weight naphthalene and sulphonated and condensed at 80° C. with 40 parts of sulphuric acid containing 18% sulphur trioxide. After cooling, 12 parts by weight of castor oil are added and condensed with 30 parts by weight of chlorosulphonic acid which latter is added gradually. The product is washed with high-percentage sodium chloride solution and neutralized partly with soda lye and partly with pyridine. It constitutes an excellent and thorough dyeing agent.

Example 3

60 parts by weight naphthalene, 50 parts by weight of olive oil, 10 parts by weight benzyl chloride and 20 parts by weight octadecenol are fused together. In the course of several hours at a temperature of 50° to 60° C., 100 parts by weight sulphuric acid containing 25% sulphur trioxide are added and then 120 parts by weight chlorosulphonic acid. The product is washed and neutralized as suggested above. The salt obtained is capable of stabilizing cotton bleaching baths containing hydrogen peroxide as bleaching agent.

Example 4

12 parts by weight castor oil are fused with 12.8 parts by weight naphthalene and then condensed with 38 parts by weight sulphuric acid containing 25% sulphur trioxide. Thereafter, 6 parts by weight of an alcohol mixture (obtained by the reduction of cocoanut fatty acids and 18.2 parts by weight butanol) are added. Finally, 40 parts by weight chlorosulphonic acid are added in small amounts. The temperature should be about 45° C. The reaction product is washed with a mixture of ice and sodium sulphate and then neutralized by potash lye. A reddish oil is obtained that is suitable for use in dyeing stockings. When mixed with dye, this compound aids in effecting penetration of the dye throughout the seams of stockings and also equalizes the dyeing action as between the artificial silk body and the cotton heel portions of silk stockings.

Example 5

60 parts by weight naphthalene, 50 parts by weight olive oil, 10 parts by weight benzyl chloride and 20 parts by weight octadecenol are mixed while stirring with 10 parts by weight phosphorus oxychloride at 60° to 80° C. until condensation (proceeding with the development of hydrochloric acid) is completed. Octadecenol phosphorus trichloride may be used in a similar way. After condensation, one reduces the temperature to 42° C. and adds chlorosulphonic acid to the condensation product with constant stirring until a good solubility in water of the reaction product, together with a strong foaming action, has been obtained. In order to obtain an electrolyte-constance of the reaction product (that is, to obtain

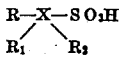
a stability such as will avoid formation of insoluble soaps by reaction of the salts with hardening elements in water), one requires 60 to 80 parts of chloro-sulphonic acid. Neutralization may be carried out in the manner described above. The reaction product is applicable to the softening of textiles (webs) after the dressing or finishing as an addition to the dressing bath.

Example 6

120 parts by weight tetrahydronaphthalene, 100 parts by weight hexadecanol and 60 parts by weight castor oil are fused together, whereupon at first at 48° C. and later at a gradually rising temperature 270 parts by weight sulphuric acid containing 25% sulphur trioxide are added in small amounts. After the reaction mixture has become fully water soluble, it is washed as usual with a concentrated solution of sodium chloride in ice and neutralized with soda lye. The condensation product obtained is an excellent wetting agent in acid and alkaline baths.

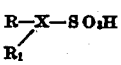
I claim:—

1. A sulphonation product of a compound obtained by condensation, said product having the general formula



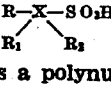
where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, R_1 represents an alkyl radical of at least 6 carbon atoms, and R_2 represents a hydrogen atom equivalent chosen from the class consisting of hydrogen and alkylating agents derived from cyclohexanol and alcohols having less than 6 carbon atoms.

2. A sulphonation product of a compound obtained by condensation, said product having the general formula



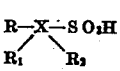
where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, and R_1 represents an alkyl radical of at least 6 carbon atoms.

3. A sulphonation product of a compound obtained by condensation, said product having the general formula



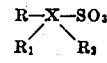
where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, R_1 represents an alkyl radical of at least 6 carbon atoms, and R_2 represents a second alkyl radical derived from the group of alkylating agents consisting of cyclohexanol, and alcohols having less than 6 carbon atoms.

4. A sulphonation product of a compound obtained by condensation, said product having the general formula



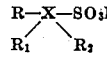
where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, R_1 represents an alkyl radical derived from the class of alkylating agents consisting of the aliphatic alcohols having at least 6 carbon atoms, and the sulphuric, phosphoric and phosphor-chloride esters of the same, and R_2 represents a hydrogen atom equivalent chosen from the class consisting of hydrogen and alkylating agents derived from cyclohexanol and alcohols having less than 6 carbon atoms.

5. A sulphonation product of a compound obtained by condensation, said product having the general formula



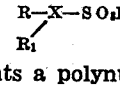
where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical derived from the group of fatty acids consisting of lauric, myristic, palmitic, stearic, oleic, elaeosteric, ricinoleic, and chlorostearic acids, and the anhydrides, halides, and esters thereof, R_1 represents an alkyl radical of at least 6 carbon atoms, and R_2 represents a hydrogen atom equivalent chosen from the class consisting of hydrogen and alkylating agents derived from cyclohexanol and alcohols having less than 6 carbon atoms.

6. A sulphonation product of a compound obtained by condensation, said product having the general formula



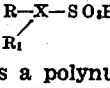
where X represents a polynuclear aromatic hydrocarbon chosen from the group consisting of naphthalene, anthracene, tetrahydronaphthalene and octahydroanthracene, R represents a higher fatty acid radical, R_1 represents an alkyl radical of at least 6 carbon atoms, and R_2 represents a hydrogen atom equivalent chosen from the class consisting of hydrogen and alkylating agents derived from cyclohexanol and alcohols having less than 6 carbon atoms.

7. A compound obtained by condensation having the general formula



where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, and R_1 represents an alkyl radical of at least 6 carbon atoms, said compound being obtained by sulphonation of the polynuclear aromatic hydrocarbon, and thereafter mixing and reacting the sulphonated hydrocarbon with a higher fatty acid and an alkylating agent chosen from the class consisting of the aliphatic alcohols having at least 6 carbon atoms, and the sulphuric, phosphoric and phosphor-chloride esters of the same, the reaction being effected at a temperature of between about 40° C. and 80° C.

8. The method for producing a compound having the general formula



where X represents a polynuclear aromatic hydrocarbon, R represents a higher fatty acid radical, and R_1 represents an alkyl radical of at least 6 carbon atoms; which method comprises sulphonating a polynuclear aromatic hydrocarbon, alkylating the sulphonated hydrocarbon with an agent chosen from the class consisting of the aliphatic alcohols having at least 6 carbon atoms, and the sulphuric, phosphoric, and phosphor-chloride esters of the same, and mixing the sulphonated and alkylated hydrocarbon with a higher fatty acid in the presence of a condensing agent.

9. The product produced by the process of claim 8.

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