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SULPHONATED HYDROCARBON  
DERIVATIVES

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This invention relates to chemical compounds, more particularly surface active substances, and a process for the manufacture thereof.

As is well known, surface active compounds which possess cleaning, wetting and dispersing properties may be advantageously used in the various industries, for example, the textile and leather industries for a wide variety of purposes. Thus, surface active compounds such as soaps, that is the sodium salts of the higher fatty acids, find a wide application in the laundering, dyeing and finishing of textiles. Soaps are characterized by the disadvantage, however, that they are not soluble in acidic solutions since the alkali metal salts of the fatty acids are converted into the insoluble fatty acids. Furthermore, in hard water the alkali metal salts of fatty acids are precipitated as the insoluble alkaline earth metal salts such as those of calcium, magnesium and the like.

While other surface active substances have been prepared, such as for example the Turkey red oils (that is, the reaction products of castor oil with concentrated sulphuric acid at relatively low temperatures) which are more soluble than soaps in the presence of mineral acids and hard water, these substances are generally much less effective detergents than the soaps they are designed to replace.

It is an object of the present invention to produce new chemical products which are highly surface active, are water soluble, and possess good wetting and detergent power even in relatively strongly alkaline or acidic solutions. A further object is the production of surface active compounds having relatively soluble alkaline earth metal salts and which, therefore, are adapted for use in hard water. A still further object of the invention is the provision of a process for producing products of the character above described. Other objects will appear hereinafter.

These objects are accomplished according to this invention whereby products especially useful as detergent, wetting and dispersing agents are produced by reacting unsaturated aliphatic hydrocarbons containing 8 or more carbon atoms and having a double bond at the end of the chain with a strong sulphonating agent and treating the resultant product with a hydrolyzing agent. Upon hydrolysis and neutralization an immiscible oil separates and may be removed from the reaction mixture by any convenient method. The remaining solution is then evaporated or otherwise treated in any suitable manner to obtain the desired product which is a highly surface active

substance, soluble in both hard and soft water, and giving solutions of excellent detergent and wetting power, stable to the addition of even strong acids or alkalis.

While the invention is susceptible of considerable variation and modification in the manner of its practical application, particularly as regards the kind and proportions of the reactants and the exact method of procedure, the following examples, in which the parts are by weight, will serve to illustrate some of the products falling within the invention and how they may be prepared.

*Example I*

Thirty parts of a mixture of olefines (B. P. 15  
245–260° C.) consisting substantially of 1-2-hexadecylene, prepared by dehydrating the appropriate fraction of primary alcohols (B. P. 190–225° C. at 65 mm.) obtained from the hydrogenation of coconut oil, were dissolved in 125  
20 parts of carbon tetrachloride and the mixture cooled to 0° C. Twenty parts of chlorosulphonic acid were then added slowly with vigorous stirring and the mixture kept cold for three hours. The reaction liquid was then treated with water  
25 and neutralized with 20% sodium hydroxide solution and 6 parts excess sodium hydroxide added. The carbon tetrachloride was steam distilled off and recovered and the residual liquid boiled  
30 for 30 minutes. The product was neutralized with 10% sulphuric acid and the immiscible oil which formed in the mixture was separated. The aqueous solution was then evaporated to a thick  
35 reddish brown oil, clearly soluble in water giving solutions of very good wetting power and stable to the addition of mineral acids, alkalis or salts of alkaline earth metals.

*Example II*

A solution was prepared from 40 parts of liquid  
40 sulphur dioxide and 20 parts of a mixture of olefines (B. P. 205–220° C.) consisting substantially of 1-2-dodecylene obtained by dehydrating a mixture of primary alcohols, in which primary lauryl  
45 alcohol was the chief constituent. To this solution was added slowly with repeated stirring a solution of 10 parts sulphur trioxide in 40 parts liquid sulphur dioxide. The resultant product  
50 was stirred for about 12 hours at –12° C. The sulphur dioxide was then removed by allowing the reaction product to warm to room temperature. The residual liquid was treated with water and then 23 parts of sodium hydroxide added. The resultant liquid was boiled for an hour and  
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neutralized with 10% sulphuric acid and the oily layer separated. The aqueous solution was evaporated to dryness giving a brown oil readily soluble in water to give solutions of considerable wetting power and stable to acids and alkalies and alkaline earth salts.

#### Example III

Twenty parts of 1-2-octadecylene obtained by dehydrating primary n-octadecyl alcohol were dissolved in about 80 parts of carbon tetrachloride and the solution cooled to about 0-5° C. Twelve parts of chloresulphonic acid were added slowly to the mixture with agitation, the resultant product being maintained at the above low temperature for a period of about 2 more hours. At the end of this time the temperature was allowed to rise to about 20-25° C. After standing at this temperature for 12-14 hours the liquid was poured into water and neutralized with 20% sodium hydroxide solution and about 6 parts excess sodium hydroxide added. The product was boiled for an hour to hydrolyze it and to remove carbon tetrachloride. The resultant product was neutralized with 10% sulphuric acid solution and the immiscible oil which formed was separated. The residual solution was evaporated to a small volume and the desired product was isolated by precipitating the inorganic salts with an excess of ethyl alcohol, filtering the alcohol solution and evaporating off the alcohol and water. The resultant product was a brown oil soluble in water, possessing good surface activity and characterized by stability, and good wetting, cleaning and dispersing power even in strongly acidic or alkaline solutions.

#### Example IV

A mixture of olefines containing 11.5 parts of the dodecylene described in Example II, and 18.5 parts of 1-2-tetradecylene (B. P. 230-245° C.) prepared by dehydrating the corresponding alcohol was reacted with a solution of 14 parts of sulphur trioxide in 30 parts of liquid sulphur dioxide. The reaction mixture was stirred for 12 hours at -12° C. and the temperature was then allowed to rise slowly to room temperature, whereupon the sulphur dioxide escaped. The product was poured into water, neutralized with 20% sodium hydroxide solution and about 5 parts of excess sodium hydroxide added. The resultant product was boiled about 1 hour to hydrolyze it, after which the solution was neutralized with 10% sulphuric acid solution and the immiscible layer of oil separated. The residual solution was then evaporated to a small volume and extracted with alcohol as described in Example III. The product was characterized by excellent wetting, cleaning and dispersing properties.

The unsaturated hydrocarbons employed in accordance with the present invention may be any aliphatic unsaturated hydrocarbons containing 8 or more carbon atoms and having a double bond at the end of the chain. Mixtures of such hydrocarbons may be employed. Or, the starting materials may be mixtures containing unsaturated hydrocarbons of the above described character and olefines in which the double linkage is not at the end of the chain. In general, the results are more desirable, however, the larger the proportion of hydrocarbons having a double linkage at the end of the chain. The aliphatic unsaturated hydrocarbons may be of the straight or branch chain type. Generally speaking, the straight chain hydrocarbons having a single bond

at the end of the chain are preferred. Hydrocarbons of this kind may be obtained in any suitable manner, for example, by dehydrating the primary alcohols obtained by hydrogenating fatty acids or their esters, e. g. those found in palm oil, tallow, coconut oil and olive oil. Branch chain unsaturated hydrocarbons falling within the invention may likewise be obtained in any desirable manner, for example, by polymerizing short chain olefines or by dehydrating synthetic higher alcohols or mixtures thereof, e. g. those produced by the hydrogenation of carbon oxides under elevated temperatures and pressures. Where branch chain hydrocarbons are employed the better results are obtained the shorter the side chain.

As previously stated, the unsaturated hydrocarbons, or mixtures thereof, should be reacted with strong sulphonating agents. By the expression "strong sulphonating agents" is meant sulphonating agents of greater sulphonating power than 100% sulphuric acid. Included among such sulphonating agents are compounds which per se have a greater sulphonating power than 100% sulphuric acid, such as, for example, sulphur trioxide, chloresulphonic acid, bromsulphonic acid, oleum and acetyl sulphuric acid. In practice, it is preferable to employ this class of sulphonating agents, and especially desirable results have been obtained with chloresulphonic acid. Where sulphur trioxide is employed, it may be introduced into the reaction mixture either in gaseous, liquid or solid form. As examples of other strong sulphonating agents may be mentioned milder sulphonating agents such as sulphuric acid in combination with reagents capable of removing water from the reaction mass, such as, for example, acetyl chloride, glacial acetic acid, acetic anhydride, propionic acid, propionic anhydride, phosphorous pentoxide, phosphorous oxychloride and boric anhydride. If desired, dehydrating agents may be employed in connection with the sulphonating agents which in themselves are strongly sulphonating, viz. sulphur trioxide, chloresulphonic acid, oleum and the like, but there appears to be very little added advantage in such a procedure.

The proportions of the sulphonating agents may vary within relatively wide limits depending largely upon the nature of the reactants. In general, it is preferable to employ about 1-2 moles of sulphonating agent for each double bond per mole of an unsaturated hydrocarbon. In certain cases, however, it may be desirable to use larger or smaller proportions of the sulphonating agent, it being understood that the desired reaction proceeds whether a small or large amount of sulphonating agent is employed.

The sulphonation may be effected in a solvent or suspension medium, that is to say, a medium which is liquid at the temperature of the reaction and is inert to the reactants or does not affect the reaction unfavorably. As examples of solvent or suspension media we may mention carbon tetrachloride, ethylene dichloride, trichlorethylene, tetrachlorethane, chloroform, liquid sulphur dioxide, diethylether, acetic anhydride, propionic acid and propionic anhydride. Generally speaking, we prefer to employ carbon tetrachloride. Solvent or suspension media are especially desirable when the sulphonating agent is sulphur trioxide.

The time allowed for the sulphonation to take place will depend largely upon the nature of the reactants and the conditions of temperature. Under ordinary operating conditions it may vary

from about 2 to 48 hours. If desired, the sulphonation may be carried on almost indefinitely. In practice, therefore, it is customary to carry out this reaction until further sulphonation has little if any effect on the results obtained.

While the temperature maintained in effecting the sulphonation may vary within relatively wide limits, the temperature employed should preferably be below that giving rise to decomposition, resinification or polymerization of the reactants and products. In general it is preferable to maintain the temperatures in this step of the process below about 50° C. and preferably within the range of about -10 to +30° C. Ordinarily higher temperatures tend to yield darker products.

The treatment of the sulphonated product to effect hydrolysis thereof may be carried out in a number of ways. Thus, water may be added until the acid concentration is relatively low and the resultant product boiled; or the sulphonated product may be neutralized and then heated with a hydrolyzing agent. In some cases it may be possible to effect hydrolysis, at least in part, by merely neutralizing the sulphonation product with an aqueous alkaline reagent and then boiling the resultant product. Hydrolyzing agents which are suitable for the practice of the invention are mineral acids, e. g. hydrochloric, sulphuric and the like or alkaline reagents, e. g. alkali metal and alkaline earth metal hydroxides. In practice we prefer to neutralize the sulphonated product with an aqueous solution of an alkali metal hydroxide, preferably sodium hydroxide and add a further quantity of the alkali metal hydroxide as a hydrolyzing agent.

The amount of the alkaline reagent employed for neutralization and hydrolysis of the sulphonation product should preferably correspond to at least one equivalent for every equivalent of the sulphonating agent used. Thus if the sulphonation is carried out with one mole of sulphur trioxide, neutralization and hydrolysis of the product may be effected with two moles of sodium hydroxide. In general it is preferable to use an excess of the alkaline reagent over the amount required for neutralization and hydrolysis.

The amount of water present during the hydrolysis may vary widely. Very satisfactory results are obtained, however, when the sulphonated product is heated with solutions of mineral acids, alkali metal hydroxides or alkaline earth metal hydroxides having concentrations of about 2-20%.

The temperature of the hydrolysis is subject to considerable variation but should preferably be above 50° C. and below the temperature at which the reactants or products decompose. A temperature of about 100° C. is normally satisfactory for carrying out the hydrolysis. If a solvent or suspension medium is used in the sulphonation, it is preferably removed prior to or during the hydrolysis by evaporation, steam distillation or in any other suitable manner.

Products of some value as emulsifying agents may be obtained by reacting unsaturated hydrocarbons of the character above described with strong sulphonating agents and then merely neutralizing the reaction mass without hydrolyzing it. These intermediate products may also possess some wetting and detergent power, particularly if relatively short chain unsaturated hydrocarbons are employed. In general, however, these products are insoluble or only slightly soluble in water, depending largely upon the sulphonating agent employed. Moreover, they do

not possess the stability to strongly acidic and alkaline solutions which characterizes the products obtained after hydrolysis.

The final products produced in accordance with the invention, on the other hand, are soluble in water. Furthermore, they are highly surface active and possess excellent cleaning, wetting and dispersing properties. They are particularly valuable from a commercial standpoint because of their stability in all kinds of acidic, alkaline and neutral aqueous media and are distinguished from any products previously prepared by their stability in strong acids and alkalies. Because of these characteristics our new products have an unusually wide application for industrial purposes. Since they may be used in acid, neutral, or alkaline baths they are especially well adapted for the laundering, dyeing, bleaching carbonizing, mercerizing and finishing of textiles. They are also well adapted for use as emulsifying and solubilizing agents for water immiscible or only slightly miscible solvents. They may be employed as such or in combination with water miscible or immiscible alcohols, ketones or other additional materials, such as washing, cleansing, emulsifying and wetting agents, e. g. trisodium phosphate, Turkey red oils, soaps, aliphatic or aromatic sulphonic acids, such as alkylated naphthalene sulphonic acids, mineral oil sulphonic acids, sulphonated derivatives of abietic acid, salts of the foregoing sulphonic acids, sulphuric esters, saponin and aliphatic and aromatic acid amides, such as sodium taurocholate or sodium salts of analogous acid amides. When employed alone or in combination with other materials such as those mentioned above they find wide application as pasting, cleansing, lathering, wetting or fulling agents in the dye, paper, textile and leather industries. The products of the invention may also be employed in combination with neutral, acid, or basic salts which serve to increase their emulsifying, wetting and dispersing power, such as, for example, sodium sulphate, sodium chloride, sodium acetate, mono-, di- and tri-sodium phosphates, sodium carbonate, sodium bicarbonate, similar compounds of the other alkali metals or of ammonium. Other additional materials with which the products of the invention may be combined are bleaching and disinfectant agents such as persulphates, percarbonates and perborates; filling materials such as talc, marble dust, starch; adsorbing material such as suitable clays, e. g. fuller's earth; protective colloids or dispersing agents such as gum tragacanth, gall acids and their derivatives, agar agar, glue, methyl cellulose, sulphite cellulose lyes, sodium cellulose phthalate, albumin, sodium cellulose glycollate, gelatin, natural and artificial resins, derivatives of cholesterol, phosphatides, gellones, natural and artificial waxes, wool waxes, solvent and softening agents, organic bases and their salts such as alkylolamine salts and quaternary ammonium compounds, inorganic colloids, alkalies, and calcium saccharate; and scouring materials such as Kieselguhr, powdered pumice, sulphur, flour, china-clay salt and the like. Desirable results for many purposes may also be obtained by employing the sulpho acids or salts thereof produced as herein described in combination with the various acyclic, monocyclic, or complex cyclic terpenes or derivatives thereof, such as, for example, limonene, dipentene, terpinolene, terpinene, phellandrene, sylvestrene, pinene, bornylene, sabinene and their alcoholic, ketonic and aldehydic derivatives. It will be apparent, fur-

thermore, our new products may be combined with a wide variety of other additional materials which possess washing, cleansing, emulsifying, wetting, dispersing, adsorbing, lathering, bleaching, germicidal and bactericidal powers. They may likewise have incorporated therewith artificial or natural perfuming substances, many of which in themselves may possess detergent properties of some value.

10 In addition to the advantages above enumerated the invention is further advantageous in that it offers a large outlet for cheap raw materials such as oils and fats from natural sources and those obtainable in large quantities as by-products from the textile, and leather industries, from fish oils, and a large number of other sources. Moreover, many of these by-products have been of relatively little value or usefulness heretofore because of the bad odor associated therewith. By converting these raw materials to olefines for use in the present process odor ceases to be a serious factor.

15 In the practical application of the products of the invention it has been noted that as a general rule their wetting properties increase with the number of carbon atoms in the unsaturated hydrocarbon employed up to about 18 carbon atoms and thereafter decrease. It has also been noted that the detergent properties of the product may vary within a relatively wide range depending largely upon the number of carbon atoms therein and the nature of the liquid in which they are employed. Thus in soft water the detergent power increases with the number of carbon atoms in the starting material and the products prepared from unsaturated hydrocarbons containing about 20-30 carbon atoms are especially desirable. In hard water, on the other hand, products prepared from unsaturated aliphatic hydrocarbons containing less than 20 but more than about 10 carbon atoms are preferred from the standpoint of detergent power. The compounds prepared from the unsaturated straight chain hydrocarbons containing about 14 to 16 carbon atoms are particularly advantageous for use in hard water.

While the chemical constitution of the products of the invention has never been definitely determined and we do not wish to be limited to any theory in this regard, in view of the enhanced wetting and detergent power of the products and their stability in strongly alkaline and acidic solutions it appears that they are most probably derivatives of true sulphonic acids.

55 As many apparent and widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or description except as indicated in the following claims.

We claim:

1. A process for preparing surface active compounds which comprises reacting an unsaturated aliphatic hydrocarbon containing at least 8 carbon atoms and having an unsaturated bond at the end of the chain, with a strong sulphonating agent until a water-soluble sulphonated hydrocarbon oil and a water-immiscible oil are formed when the sulphonation product is heated with a hydrolyzing agent and neutralized, then heating the sulphonation reaction product with a hydrolyzing agent, neutralizing and recovering the water-soluble sulphonated hydrocarbon oil from the hydrolysis product substantially free from the water-immiscible oil.

2. The process of claim 1 in which the sulphonation is effected in the presence of a solvent or suspension medium.

3. The process of claim 1 in which the sulphonating agent is chlorosulphonic acid.

4. The process of claim 1 in which the proportions of sulphonating agent correspond to about 1 to 2 moles for each double bond per mole of unsaturated hydrocarbon.

5. The process of claim 1 in which the sulphonation reaction is carried out at a temperature within the range of about  $-10^{\circ}\text{C.}$  to  $+35^{\circ}\text{C.}$

6. The process of preparing surface active compounds which comprises reacting an unsaturated aliphatic hydrocarbon containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulphonating agent until a water-soluble sulphonated hydrocarbon oil and a water-immiscible oil are formed when the sulphonation product is heated with an excess of an aqueous alkali metal hydroxide solution and neutralized, then heating the said sulphonation product with an excess of an aqueous alkali metal hydroxide solution, neutralizing, separating the water-immiscible oil, and recovering the water-soluble sulphonated hydrocarbon oil.

7. The process of claim 6 in which the water-soluble hydrocarbon residue is recovered substantially free from inorganic salts.

8. The process of preparing products which are highly surface active, possess excellent detergent and wetting power, are stable in acid, neutral and alkaline solutions, and which are most probably hydroxy sulphonic acid derivatives of aliphatic hydrocarbons, which comprises reacting an unsaturated aliphatic hydrocarbon containing 10 to 18 carbon atoms and having only one double bond which is at the end of the chain, with a strong sulphonating agent until a water-soluble sulphonated hydrocarbon oil and a water-immiscible oil are formed when the sulphonation product is heated with an excess of an aqueous sodium hydroxide solution and neutralized, then boiling said sulphonation reaction product with an excess of an aqueous sodium hydroxide solution, neutralizing the resulting product, separating the water-immiscible oil, and recovering the water-soluble sulphonated hydrocarbon oil.

9. The process as claimed in claim 8 in which the water-soluble sulphonated hydrocarbon oil is recovered substantially free from inorganic salts.

10. The process of preparing products which are surface active, possess detergent and wetting power, are stable in acid, neutral and alkaline solutions, and are most probably hydroxy sulphonic acid derivatives, which comprises reacting a branched chain, unsaturated aliphatic hydrocarbon containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulphonating agent until a water-soluble sulphonated hydrocarbon oil and a water-immiscible oil are formed when the sulphonation product is heated with an aqueous alkali metal hydroxide solution and neutralized, then heating said sulphonation reaction product with an excess of an aqueous alkali metal hydroxide solution, neutralizing the resultant product, separating the water-immiscible oil, and recovering the water-soluble sulphonated hydrocarbon oil.

11. A process of producing products which are highly surface active, possess excellent detergent and wetting power, are stable in acid, neutral and alkaline solutions, and are most probably hydroxy sulphonic acid derivatives, which comprises

reacting an unsaturated aliphatic hydrocarbon containing 8 to 18 carbon atoms and having only one double bond which is at the end of the chain, with sulphur trioxide in the presence of liquid sulphur dioxide as a solvent until a water-soluble sulphonated hydrocarbon oil and a water-immiscible oil are formed when the solvent is allowed to evaporate and the sulphonation product is heated with an excess of an aqueous sodium hydroxide solution and neutralized, then evaporating the solvent, boiling the residual sulphonation reaction product with an excess of an aqueous sodium hydroxide solution, neutralizing the resultant product, separating the water-immiscible oil, and recovering the water-soluble sulphonated hydrocarbon oil.

12. A process for preparing surface active substances which comprises reacting a mixture of olefines preponderating in 14 to 16 carbon atom olefines boiling within the range of about 230° C. to about 260° C., obtainable by the dehydration of the appropriate fraction of coconut oil alcohols, with a strong sulphonating agent until a water-soluble sulphonated hydrocarbon oil and a water-

immiscible oil are formed when the sulphonation product is heated with a hydrolyzing agent and neutralized, then heating the sulphonation reaction product with a hydrolyzing agent, neutralizing, and recovering the water-soluble sulphonated hydrocarbon oil from the hydrolysis product substantially free from the water-immiscible oil.

13. The process of claim 12 in which the olefine mixture is an olefine fraction boiling within the range of 245° C. to 260° C.

14. The process which comprises reacting an aliphatic unsaturated hydrocarbon containing at least eight carbon atoms and having a double bond at the end of the chain with a sulphonating agent at a temperature below about 50° C. in the presence of an inert solvent for the unsaturated hydrocarbon, then removing the solvent, heating the remaining product with a hydrolyzing agent, neutralizing the resultant product whereby an immiscible oil forms in the reaction mixture, removing said oil, and recovering the water-soluble sulphonic acid residue.

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