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SULPHONATED DERIVATIVES OF ALIPHATIC HYDROCARBONS USEFUL AS WETTING AND CLEANSING AGENTS

Frederick Baxter Downing, Carneys Point, N. J.,
and Richard Gesse Clarkson, Wilmington, Del.,
assignors to E. I. du Pont de Nemours & Company,
Wilmington, Del., a corporation of Delaware

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

It is known that 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. Soaps are also precipitated in strongly alkaline solutions. Moreover, in hard water the alkali metal salts of the higher 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.

The present invention has for an object the production of new chemical products which are highly surface active. A further object is to produce compounds which are water soluble and possess good wetting and detergent power even in relatively strongly alkaline or acidic solutions and which, therefore, are adapted for use in acidic, neutral or alkaline baths. Another object is the production of surface active compounds having relatively soluble alkaline earth metal salts. A still further object of the invention is the provision of a new and improved process for producing the above described products. A further object is the production of compounds of the character described by a direct process involving reactions which proceed smoothly to produce the desired products in a high state of purity and in almost theoretical yields. Further 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 in the presence of a sulphonating catalyst and treating the reaction product with a hydrolyzing agent.

While the invention is subject to considerable variation and modification in the manner of its practical application, particularly as regards the kind and proportion 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

Twenty parts of 1-2-octadecylene (B. P. 180–205° C. at 30 mm. Bromine No. 64.7) obtained by dehydrating substantially pure primary n-octadecyl alcohol were dissolved in about 80 parts of carbon tetrachloride. Approximately one-tenth part of mercurous sulphate was suspended in the solution which was then cooled to about 0–5° C. Twelve parts of chlorsulphonic acid were added slowly to the mixture with agitation, the resultant mixture 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 about 12–14 hours the liquid was poured into water, neutralized with 20% sodium hydroxide solution and about 10 parts of excess sodium hydroxide added. The product was boiled for one hour to hydrolyze it and to remove carbon tetrachloride. The resultant solution was neutralized with 10% sulphuric acid solution and then evaporated to a small volume. The 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 light brown oil, clearly soluble in water and possessing high surface activity. It was stable and was characterized by marked cleaning, dispersing and penetrating power even in aqueous solutions containing more than 10% of a mineral acid or alkali metal hydroxide such as, for example, hydrochloric acid and sodium hydroxide. In fact, no tendency towards instability was noticed in any alkaline, neutral or acidic aqueous solutions. The weight of product obtained in the foregoing manner was about 27.2 parts.

Example II

1-2-octadecylene was reacted with chlorsulphonic acid and the resultant product was hydrolyzed as described in Example I, except that one-tenth part of silver sulphate was used as a

catalyst instead of mercurous sulphate. The yield of product obtained by extraction with alcohol was about 26.4 parts. An aqueous solution of the product was perfectly clear and possessed excellent detergent and wetting properties.

Example III

Thirty parts of 1-2-hexadecylene (Bromine No. 72.6) obtained by dehydrating substantially pure n-hexadecyl alcohol were dissolved in about 120 parts of carbon tetrachloride. About one-tenth part of mercurous sulphate was suspended in the solution which was then cooled to about 0-5° C. 39.6 parts of oleum containing 65% sulphur trioxide were added slowly with agitation. The resultant product being maintained at the above low temperature (0-5° C.) for about 2-3 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, neutralized with 20% sodium hydroxide solution and about six parts of excess sodium hydroxide added. The product was boiled for an hour to hydrolyze it and to remove carbon tetrachloride. The resultant solution was neutralized with 10% sulphuric acid solution, then evaporated to a small volume and recovered substantially free from inorganic salts by extraction with ethyl alcohol, as described in Example I. The resultant product possessed high surface activity and was characterized by unusual stability in combination with marked wetting, cleaning, and dispersing power even in strongly acid or alkaline solutions. The weight of product obtained in this way was about 41.5 parts.

Example IV

A mixture of olefines was prepared by mixing together 11.5 parts of 1-2-dodecylene (obtained by dehydrating substantially pure lauryl alcohol) and 18.5 parts of 1-2-tetradecylene (prepared by dehydrating a corresponding alcohol). To this mixture was added a solution of 14 parts of sulphur trioxide in 30 parts of liquid sulphur dioxide and about one tenth part of mercurous sulphate. The reaction mixture was stirred for about 12 hours at -12° C. and the temperature then allowed to rise slowly to about 20-25° C.

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 one hour to hydrolyze it after which the solution was neutralized with 10% sulphuric acid, evaporated to a small volume and then extracted with alcohol as described in Example I. The final product was characterized by excellent wetting, cleaning and dispersing properties, the yield obtained being about 21 parts.

For comparison, the procedures described in Examples I, II, and IV were carried out without a catalyst, all other conditions of operation and proportions of materials being the same. In marked contrast with the reactions where a catalyst was used, it was observed that after hydrolysis and neutralization of the hydrolyzed product with the 10% sulphuric acid solution an oily liquid formed in the reaction mixture. This oily substance was removed and the remaining liquid evaporated to a small volume and extracted with alcohol as described in Example I. The average yield of product obtained according to the procedures of Examples I and II, without a catalyst, was about 23.0 parts and that obtained

according to the procedure of Example IV, without a catalyst, was about 16 parts. While these products were soluble in water and possessed good wetting, cleaning and dispersing properties even in relatively strongly acidic or alkaline solutions, it will be apparent that the yield was not so high as that obtained from the reactions with a catalyst. Thus, the increase of yield obtained by the procedure of Example IV was about 31%. Actually the increase in the yields in each case was probably greater than that shown by the foregoing figures since the products obtained by the use of catalysts were purer than those obtained without catalysts. This was shown by the fact that aqueous solutions of the products obtained with catalysts were perfectly clear while solutions of the products obtained without a catalyst were cloudy, the cloudiness probably indicating incomplete removal of the byproduct oily material formed during the hydrolysis. Furthermore, it should be noted that the products obtained from the reactions with a catalyst were more effective wetting agents than the products obtained without catalysts.

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 character above described 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 branched chain type. Generally speaking, the straight chain hydrocarbons having a single double 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 contained in palm oil, tallow, coconut oil and olive oil. Branched chain unsaturated hydrocarbons falling within the invention may likewise be obtained in any desirable manner, for example, by polymerizing relatively 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 branched chain hydrocarbons are employed the better results are obtained the shorter the side chain.

The expression "strong sulphonating agents" is used herein to mean 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, chlorosulphonic acid, bromsulphonic acid, oleum and acetyl sulphuric acid. In practice, it is preferable to employ this class of sulphonating agents, and very desirable results have been obtained with chlorosulphonic acid, oleum and sulphur trioxide. 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 capa-

ble of removing water from the reaction mass, such as, for example, acetyl chloride, glacial acetic acid, acetic anhydride, propionic acid, propionis anhydride, phosphorus pentoxide, phosphorus 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, chlorosulphonic 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 larger amount of sulphonating agent is employed.

As indicated by the examples, the reaction of the sulphonating agent with the unsaturated hydrocarbon is preferably effected in a suitable liquid medium, that is to say, a medium which is liquid at the temperature of the reaction and is inert to the reactants and products or does not affect the reaction unfavorably. It may or may not be a solvent for the reactants and/or products. As examples of such media may be mentioned carbon tetrachloride, ethylene-dichloride, trichlorethylene, tetrachlorethane, chloroform, liquid sulphur dioxide, diethyl ether, acetic anhydride, propionic acid and propionic anhydride. Generally speaking, we prefer to employ solvent or suspension media having a boiling point below about 100° C., and especially desirable results have been obtained with carbon tetrachloride. Solvent or suspension media are particularly advantageous when the sulphonating agent is sulphur trioxide.

The catalyst employed in accordance with the invention may be any catalyst favoring the sulphonation of carbon compounds. The catalyst should preferably be soluble in the reaction mixture and, furthermore, should preferably be a compound which does not give rise to oxidation reactions. As examples of sulphonating catalysts may be mentioned boric anhydride, mercuric sulphate, mercurous sulphate, mercurous oxide, mercuric oxide, silver sulphate, silver acetate and silver oxide. It will be recognized that the results obtained with the foregoing catalysts may differ widely depending largely upon the specific reactants and conditions of operation. Of the various sulphonating catalysts with which we have practiced the invention the results obtained with mercurous sulphate and silver sulphate have been very advantageous.

The amount of catalyst employed may vary considerably depending more or less upon the nature thereof and that of the reactants, but as a general rule desirable results have been obtained by the addition of catalysts to the reaction mixture in proportions corresponding to about 0.1-5.0% by weight of the reacting substances.

The time allowed for the reaction between the sulphonating agent and the unsaturated hydrocarbon to take place will depend largely upon the nature of the reactants, the catalysts and the conditions of temperature. Under ordinary operating conditions it may vary from about 2 to 48 hours. In practice this reaction is ordi-

narily allowed to proceed until further sulphonation causes no substantial change in the character of the results obtained.

While the temperature maintained in effecting the sulphonation reaction 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-+35° C. Ordinarily, higher temperatures tend to yield darker products.

The hydrolysis of the product resulting from the reaction of the sulphonating agent and the unsaturated hydrocarbon may be effected 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 reaction product of the sulphonating agent and unsaturated hydrocarbon 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 heat the product with a further quantity of the alkali metal hydroxide to effect hydrolysis.

The amount of alkaline reagent employed for neutralization and hydrolysis of the sulphonation product should preferably correspond to at least one equivalent for every equivalent of sulphonating agent used. Thus, if the reaction with the unsaturated hydrocarbon is carried out by means of 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 first step of the process, it is preferably removed prior to or during hydrolysis by evaporation, steam distillation or in any other suitable manner. The time allowed for the hydrolysis is preferably determined by allowing the hydrolytic action to proceed until a sample of the product dissolves in water.

Products of some value as emulsifying agents may be obtained by reacting the unsaturated aliphatic hydrocarbons with a strong sulphonating agent in the presence of a sulphonating catalyst as above described, and then merely neutralizing the reaction product 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.

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 alkalis. 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, sulphuric esters, saponin and aliphatic and aromatic acid amides, such as sodium taurocholate or sodium salts of analogous acids 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, and 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, and starch; adsorbing materials 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, calcium saccharate, albumin, sodium cellulose glycollate, gelatin, natural and artificial resins, derivatives of cholesterol, phosphatides, gelloses, 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, and alkalis; 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, furthermore, 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.

In addition to the advantages above enumerated the invention is further advantageous in that it offers a large outlet for cheap raw material 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.

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, and those prepared from the unsaturated straight chain hydrocarbons containing about 14 to 16 carbon atoms are particularly advantageous.

The chemical constitution of the products produced in accordance with the invention has not been definitely determined and, therefore, we do not wish to be limited by any theory in this regard or in regard to the mechanism of the reactions. In view of the enhanced wetting and detergent power of these products and their greater stability in strongly alkaline and acidic solutions than products previously prepared, it appears that they are most probably true sulphonic acid derivatives. It does not necessarily follow, however, that the chemical constitution of the products is the same regardless of the sulphonating agent used in the process. Thus, the products resulting when the sulphonation is carried out with oleum may differ in chemical structure from those obtained when chlorosulphonic acid is the sulphonating agent. The nature of the catalyst may also have a directive influence on the reaction. In a process which includes the step of reacting unsaturated hydrocarbons of the character herein described with a halogen sulphonic acid in the presence of a halogenating catalyst, the results obtained are very highly advantageous. Comparative tests have shown, however, that there is no apparent advantage in reacting oleum with unsaturated hydrocarbons in the presence of halogenating catalysts such as pyrolusite since upon hydrolysis and neutralization of the reaction product an immiscible oil forms in the reac-

tion mixture just as if no catalyst had been used.

As will be apparent the process herein described involving the use of a sulphonating catalyst is advantageous over a similar procedure in which no catalyst is used in that the yield of product is higher and the step of separating the by-product oil formed upon hydrolysis and neutralization is eliminated. Furthermore, as previously pointed out, the products obtained by reaction of the unsaturated hydrocarbon with a strong sulphonating agent in the presence of a sulphonating catalyst and then hydrolyzing are somewhat better than those obtained by a similar procedure without a catalyst.

It is believed that the products of the invention are most probably hydroxy sulphonic acid derivatives of aliphatic hydrocarbons, in which a hydroxy group and a sulphonic acid residue occur on the last two carbon atoms of an aliphatic chain having 8 or more carbon atoms. It is not known whether the sulphonic acid group or the hydroxy group occurs on the alpha carbon atom of the hydrocarbon chain. Possibly the products may be isomeric mixtures of compounds in which the sulphonic acid residue occurs on the alpha carbon atom and those in which it occurs on the beta carbon atom, depending upon the specific sulphonating agent used, the unsaturated hydrocarbons reacted upon and the specific sulphonating catalysts. If the unsaturated hydrocarbon reacted upon has an unsaturated bond at the end of the hydrocarbon chain and also in another portion of the chain, it is possible that a hydroxy group and a sulphonic acid residue will be introduced at this unsaturated bond also. As already indicated, however, the products obtained from straight chain hydrocarbons having a single unsaturated bond at the end of the chain possess superior properties to those in which an unsaturated bond occurs in the middle of the chain.

As many 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 substances, which comprises reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulphonating agent in the presence of a sulphonating catalyst of the class consisting of inorganic oxides and salts of silver, and hydrolyzing the reaction product.

2. A process for preparing surface active substances, which comprises reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the end of the chain, with chloresulphonic acid in the presence of a sulphonating catalyst of the class consisting of inorganic oxides and salts of silver and hydrolyzing the reaction product.

3. A process for preparing surface active substances, which comprises reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the

end of the chain, with a strong sulphonating agent in an inert solvent reaction medium, and in the presence of a sulphonating catalyst of the class consisting of inorganic oxides and salts of silver, and hydrolyzing the reaction product.

4. The process of producing a highly surface active substance, which comprises reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulphonating agent at a temperature within the range of about -10 to $+35^{\circ}\text{C}$., in an inert solvent reaction medium, in the presence of a sulphonating catalyst of the class consisting of inorganic oxides and salts of silver, then removing the reaction medium, heating the remaining product with a hydrolyzing agent, neutralizing the resultant product and recovering the neutralized product.

5. The process of preparing surface active substances, which comprises reacting a straight chain unsaturated aliphatic hydrocarbon, containing at least 8 carbon atoms and having a single double bond at the end of the chain, with chloresulphonic acid in proportions corresponding to about 1 to 2 moles of chloresulphonic acid per mole of unsaturated hydrocarbon, in an inert solvent reaction medium boiling below about 100°C ., at a temperature within the range of -10 to $+35^{\circ}\text{C}$., in the presence of silver sulphate, adding to the resultant product water and about one equivalent of alkali metal hydroxide for every equivalent of chloresulphonic acid used, the proportions of water corresponding to an aqueous solution of said alkali metal hydroxide having a concentration of about 2-20%, heating the product obtained to a temperature of about 100°C ., to effect hydrolysis thereof and at the same time to remove the reaction medium, neutralizing the hydrolyzed product with a mineral acid and recovering the neutralized product substantially free from inorganic salts.

6. A process for preparing surface active substances which comprises reacting a straight chain aliphatic unsaturated hydrocarbon containing at least 8 carbon atoms and having a single double bond at the end of the chain, with a strong sulphonating agent in the presence of a sulphonating catalyst of the class consisting of inorganic oxides and salts of silver, and hydrolyzing the reaction product.

7. In a process of preparing surface active substances, the step which comprises reacting an olefine containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulphonating agent in the presence of a catalyst of the class consisting of inorganic oxides and salts of silver.

8. Hydroxy sulphonic acids of aliphatic hydrocarbons and salts thereof, in which a hydroxy group and a sulphonic acid residue occur on the last two carbon atoms of an aliphatic chain containing more than 20 and less than 30 carbon atoms, said products being characterized by excellent detergent power in soft water.

FREDERICK B. DOWNING.
RICHARD G. CLARKSON.