

UNITED STATES PATENT OFFICE

1,968,797

SULPHURIC DERIVATIVE OF HIGHER ALCOHOLS

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No Drawing. Application January 4, 1933, Serial No. 650,203. In Germany March 30, 1928

18 Claims. (Cl. 260—99.12)

This invention relates to soap-like products and to the manufacture of soaps, detergents, and the like, and to improvements in treatment liquids for use in the textile, leather, and allied industries. It is the primary object of the invention to produce new soap-like materials and other substances of this character having greater wetting, cleansing, dispersing, and foaming properties than the agents heretofore used.

Water-soluble sulphuric esters produced by the action of sulphuric acid on fatty materials, including both fatty acids and esters of fatty acids, containing double linkages and/or hydroxyl groups, are widely employed as wetting, cleansing, and dispersing agents in the textile and related industries. Thus a sulphuric acid ester of the hydroxy stearic acid may be produced by treating oleic acid with sulphuric acid, and a sulphuric acid ester of a dihydroxy stearic acid may be obtained by the treatment of ricinoleic acid with sulphuric acid. These agents are not entirely satisfactory, since sulphated fatty materials heretofore available contain carboxyl groups—either free or combined with alkali, depending upon the proportion of alkali used for neutralization after sulphonation—and in consequence are capable of forming insoluble alkali earth salts. For instance, the difficultly soluble lime salts of these esters produce deleterious effects in the textile industry.

In accordance with the present invention, this defect is in large measure avoided if, instead of fatty acids or the esters of these acids, the corresponding alcohols obtained therefrom by replacement in effect of the carboxyl group whether free or combined with the CH_2OH group are treated with sulphuric acid or with other sulphonating or sulphonating agent. Commercial fats are essentially mixed glycerides of the various higher fatty acids, and the higher alcohols obtainable therefrom are mixtures of alcohols of the general formula $\text{C}_x\text{H}_y-\text{CH}_2\text{OH}$. These mixtures consist predominantly of alcohols having 10 or more carbon atoms per molecule, corresponding to the molecular weight of the fatty acids, free or combined, contained in the natural fats and fatty oils and the other commercially available fatty materials derived therefrom. I have found that products soluble in water and valuable for use as wetting, cleansing, dispersing, and foaming agents can be obtained by treating such alcohols with sulphuric acid or with other sulphonating or sulphonating agent. These alcohols may be referred to collectively as nor-

mal primary alcohols having more than eight carbon atoms to the molecule.

Thus the invention contemplates the conversion of the free or combined fatty acids of fatty materials, i. e. animal and vegetable fats and oils, and manufactured derivatives such as oleic acid or ethyl oleate, into the corresponding alcohols, and the treatment of these alcohols with a sulphonating or sulphonating agent such as sulphuric acid. Usually it is also advisable to neutralize the reaction product with a base, for example sodium hydroxide or ammonia to form a water soluble soap-like salt, as is common practice in the case of sulphated fatty acids or sulphated fatty oils, such as Turkey red oil.

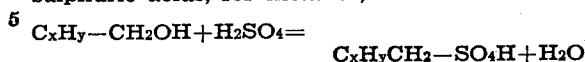
The precise nature of the method selected to convert the fatty material to the alcohol may be varied. For instance, a well-known method is that of Bouveault and Blanc, in accordance with which an alkyl ester of a fatty acid, e. g. an ethyl oleate, is reduced by sodium or other alkali metal and a lower aliphatic alcohol such as butyl alcohol, or the improved method described in my application for Letters Patent Serial No. 472,764 may be used. Numerous processes are known for preparing the alkyl esters from fats and fatty acids.

The Bouveault and Blanc process is of general application for the preparation of both unsaturated and saturated alcohols. For instance, by this process oleic alcohol ($\text{C}_{17}\text{H}_{33}-\text{CH}_2\text{OH}$) may be prepared from esters of oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$). An octodecyl alcohol ($\text{C}_{17}\text{H}_{35}-\text{CH}_2\text{OH}$) may be formed from esters of stearic acid ($\text{C}_{17}\text{H}_{35}-\text{COOH}$). Mixed saturated and unsaturated alcohols result when the unfractionated esters of the fatty acids of most natural fats, for example, tallow, are reduced according to the Bouveault and Blanc process.

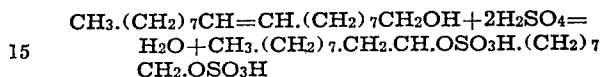
An important example of a method for preparing predominantly saturated alcohols is catalytic hydrogenation of esters under high pressure, as described in the application for U. S. Letters Patent of Wilhelm Normann, Serial No. 510,326, filed January 21, 1931, and assigned to the assignee of the present application. This method may be applied directly to the conversion of the natural glycerides, such as coconut oil, to primary alcohols for use in accordance with the present invention.

Fatty alcohols obtained from the source described are next treated with a sulphonating agent having water-binding properties. Ordinary concentrated sulphuric acid may be used, or stronger reagents such as anhydrous sulphuric acid,

chlorsulphonic acid, or fuming sulphuric acid. The principal reaction occurring is the formation of sulphuric esters, frequently called alkyl sulphuric acids, for instance, as follows:



In the case of an unsaturated alcohol, some addition of sulphuric acid at the double bond also occurs, so that complete reaction of sulphuric acid with oleic alcohol would be according to the equation:

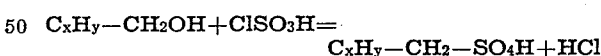


sulphuric ester of 1, 9-octodecanediol.

Unless a higher temperature is required to melt the alcohol, I prefer to effect sulphation in the cold within the range of ordinary room temperature or lower, down to about 0° C. However, higher and lower temperatures can be used, and my invention is not restricted to a particular range of temperature of sulphation.

Under almost any practical condition of sulphation, there may be formed at least traces of sulphonic acids, the proportion of which may be increased by choice of sulphating medium and other conditions of reaction, for instance, by high reaction temperatures and by the use of highly concentrated energetically acting reagents such as fuming sulphuric acid. While these are not my preferred reaction conditions, it should be understood that the sulphation products made in accordance with the present invention are not purely esters, but may contain also appreciable amounts of sulphonic acids or sulphonates. For convenience, the products resulting from the treatment with sulphuric acid or other agent hereinbefore mentioned will be referred to generically as "sulphuric reaction products".

One method of sulphating which is of fairly general application to different alcohol mixtures is to treat the alcohol just above its melting point with 100%–110% of the theoretical quantity of chlorsulphonic acid required according to the equation



The acid reaction products obtained as described above are preferably carefully neutralized, for instance, with sodium hydroxide. Neutralization should be carried out at relatively low temperatures, preferably in a vessel fitted with a means for cooling. The resulting organic salts such as sodium lauryl sulphate may be separated from inorganic components such as sodium sulphate and sodium chloride by known methods, for instance, by dissolving in ethyl alcohol, decanting or filtering, and evaporating off the solvent. With or without this purification, the products obtained are in general readily soluble in water, possess marked wetting, cleansing, dispersing, and foaming properties, and may be employed for manifold textile purposes. In a general way, they resemble the ordinary commercial sulphuric esters of the fats and fatty acids, but are greatly superior in resistance to precipitation by lime salts and the other characteristic constituents of hard water.

The sulphated products of oleic alcohol are particularly resistant to hardness and are high-

ly suitable for use in the textile and related industries.

Likewise a high resistance to the action of hard water is shown by the sulphated products of lauryl alcohol, which is the principal constituent of the mixed alcohols obtained by reduction of coconut, palm kernel and similar oils, or by reduction of the alkyl esters or the free fatty acids of these oils. Sulphated alcohols of this class have remarkable cleansing and foaming properties, and are valuable as soap substitutes, especially for use in hard water.

The sulphuric reaction products derived from lauryl alcohol, especially the esters and salts thereof, are also found to be particularly effective in the textile industry. Thus when starting from the fatty alcohols made from free fatty acids of the coconut oil or palm seed oil in a manner known per se by esterifying the fatty acids of the same with lower aliphatic alcohols and reducing the mixture of esters by means of sodium, it is advantageous to distill the reduction product and to use only the first 50% to 60% of the distillate. The product thus obtained consists mainly of lauryl alcohol, the somewhat less suitable higher fractions which contain principally myristyl alcohol and octodecyl alcohol being substantially eliminated. It should be understood, however, that the presence of the sulphuric derivatives of lower or higher alcohols, such as of myristyl alcohol with the lauryl alcohol derivatives does not materially decrease the efficiency of the final product.

Various other higher alcohols may be produced and converted into wetting and cleansing agents, substantially according to the procedure indicated in the above examples, for instance the following:

Alcohols obtained by catalytic hydrogenation of the free fatty acids of coconut oil and comprising mainly lauric alcohol, myristic alcohol, cetyl alcohol, and stearic alcohol or the single alcohols separated from each other by fractional distillation.

Alcohols obtained by catalytic hydrogenation of palm kernel oil or of the free fatty acids of palm kernel oil comprising similar constituents as the alcohols obtained from coconut oil.

Alcohols obtained by saponification of spermaceti, sperm oil, beeswax and distillation according to Axelrad and Hochstadter (U. S. A. Patent 1,290,870).

Linoleic alcohol obtained by reduction of linoleic acid by means of sodium and ethyl alcohol.

Alcohols obtained by catalytic reduction of tallow or the free fatty acids of tallow.

Alcohols obtained by catalytic hydrogenation of the free fatty acids of coconut oil.

Alcohols obtained by catalytic hydrogenation of the free fatty acids of palm kernel oil.

Alcohols obtained by reducing olive oil by means of metallic sodium and butyl alcohol.

Alcohols obtained by reducing the ethyl esters of tallow fatty acids by means of metallic sodium and butyl alcohol.

Alcohols obtained by catalytic hydrogenation of the ethyl ester of commercial stearic acid.

Ricinoleic alcohol obtained by reduction of ricinoleic acid by means of sodium and ethyl alcohol.

The following examples are given to illustrate the manner in which the process may be carried out:

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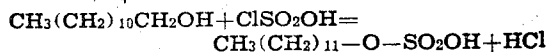
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Example 1

100 kgs. of a mixture of fatty alcohols mainly consisting of lauryl alcohol, and obtained from coconut oil by esterification of the fatty acids with ethyl alcohol, reduction of the ethyl ester, distillation of the product of the reduction and collection of the first 50% to 60% of the distillate, are heated to melting temperature about 30° C. and treated at this temperature with 50 kgs. of chlorosulphonic acid.

The foregoing reaction may be represented by the following formula:



100 kgs. of pure lauryl alcohol would require for best results a higher proportion of chlorosulphonic acid about 60 kgs.

Example 2

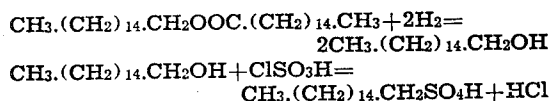
100 kgs. of the same mixture of fatty alcohols is sulphonated with 70 kgs. of fuming sulphuric acid 10% SO_3 at the temperature of 50° C.

The products of the reaction are directly neutralized by means of soda lye and separated by known methods from inorganic components such as sodium sulphate or sodium chloride.

Example 3

100 kgs. of a mixture of fatty alcohols obtained by catalytic reduction of spermaceti with hydrogen and a copper catalyst at a temperature between 300 and 350° C. and a pressure of 150-200 atmospheres until the acid number has wholly disappeared, are sulphonated at a temperature of 35° C. with 60 kgs. of chloro-sulphonic acid. The product is poured in 200 kgs. of ice water and is then neutralized by means of a potassium hydroxide solution. There results a white paste readily soluble in water.

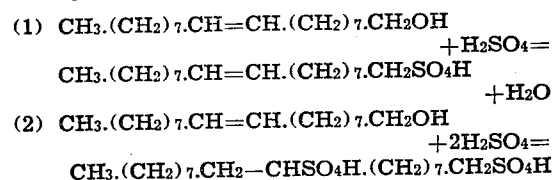
The reactions occurring can be represented by the following equations:



Example 4

100 kgs. of oleic alcohol are sulphated at 25° C. with 80 kgs. of concentrated sulphuric acid. The mixture is poured into 150 kgs. of ice water and is neutralized by means of piperidine.

The reaction may be represented by the following equations:

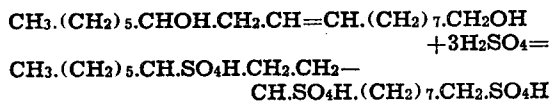


Example 5

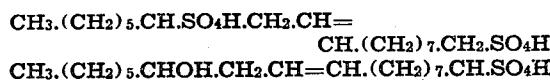
100 kgs. of the mixture of unsaturated and saturated fatty alcohols obtained by reduction of coconut oil by means of an alkali metal and butyl alcohol, adding water, separating the resulting watery alkali hydroxide solution and removing the butyl alcohol by distillation, are treated with 80 kgs. of chlorosulphonic acid at 35° C. The product is worked up as described in Example 3, neutralized with sodium hydroxide solution to form a white, readily water-soluble paste.

Example 6

100 kgs. of ricinoleic alcohol obtained by reduction of ricinoleic acid by means of sodium and amyl alcohol, adding water, separating the watery alkali hydroxide solution and removing the amyl alcohol by distillation are treated with 150 kgs. of concentrated sulphuric acid at a temperature between 10 and 20° C. The product is worked up as described in Example 3 and neutralized by means of equal parts of sodium hydroxide solution and potassium hydroxide solution. An oily product readily soluble in water is obtained. The main reaction is probably represented by the following equation:

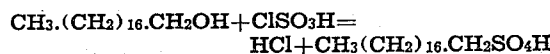


Besides this reaction there may be also a reaction of only two or only one of the free groups (two hydroxyl groups and one double linkage) capable of reaction with sulphating means. These reactions yield for example the following products



Example 7

100 kgs. of stearic alcohol are treated at 40-50° C. with 50 kgs. of chlorosulphonic acid. The product is worked up as described in Example 3. A white paste is obtained. The reaction can be represented by the following formula:



Example 8

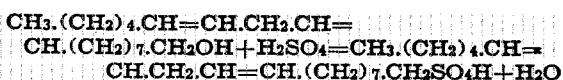
100 kgs. of a mixture of the alcohols obtained by saponification of spermaceti oil by means of caustic lime and distillation of the saponification product according to U. S. A. Patent 1,290,870, said alcohols having an iodine number of about 50 and consisting mainly of cetyl alcohol and oleic alcohol, are mixed with 100 kgs. of concentrated sulphuric acid at 40° C. The mass is then poured into 200 kgs. of ice water. The mixture is neutralized by adding sodium hydroxide solution of 28° Bé. The resulting solution containing 15-20% calculated on free fatty alcohol, is introduced in a spraying dryer of the Krause system and dried at a temperature between 75-80° C., the temperature of the hot air entering at the bottom of dryer being about 170° C.

Before or after the drying operation such quantities of Glauber's salt may be added to the solution or to the dried product respectively, that the final product contains for example 35% calculated on free fatty alcohol.

Example 9

100 kgs. of linoleic alcohol obtained by reduction of linoleic acid by means of an alkali metal and ethyl alcohol in a manner known per se, are dissolved in 50 kgs. of water free ethyl ether and treated with 200 kgs. of concentrated sulphuric acid at a temperature between 0 and 5° C. for several hours. The product is mixed with 300 kgs. chopped ice and 50 kgs. ethyl ether, washed with saturated Glauber's salt solution and neutralized by means of triethanolamine.

The reaction is probably represented by the following equation:



5 Besides the esterification of the CH_2OH group also addition of sulphuric acid to one or both of the double linkages may occur.

The following fatty materials have been found particularly suitable for conversion to alcohols and thence to sulphuric acid derivatives: tallow, 10 lard, whale oil, coconut oil, palm kernel oil, palm oil, olive oil, castor oil, linseed oil, tall oil, technical stearic acid, technical oleic acid and ricinoleic acid, palmitic acid, tallow fatty acids, Japan wax, spermaceti, sperm oil, beeswax, Montan wax, methyl, ethyl, propyl and butyl esters of 15 technical fatty acid mixtures such as stearic acids, oleic acids, tallow fatty acids, linseed oil fatty acids and whale oil fatty acids.

20 The present invention is disclosed in my prior applications Serial Nos. 350,135, filed March 26, 1929, and 433,815 filed March 6, 1930, of which the present application is a continuation in part.

25 It is to be understood that this invention is not limited to the specific embodiments hereinbefore disclosed, but that it includes all modifications as to procedure and all equivalent materials coming within the terms of the claims and the scope or the tenor of the specification.

30 Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. In the manufacture of soap-like materials, the combined steps of converting the carboxyl groups of a fatty material to primary alcohol groups and then reacting the resulting alcohols with a sulphonating agent.

35 2. A soap-like material comprising essentially salts of alkyl sulphuric acids derived from primary alcohols resulting from the reduction of the fatty acid radicals contained in fatty material.

40 3. A wetting and cleansing agent comprising essentially water-soluble sulphuric esters of alcohols obtained by sulphation of fatty material from which carboxyl groups, including combined carboxyl groups, are eliminated.

45 4. A wetting and cleansing agent comprising essentially a water-soluble sulphonation product of primary alcohols resulting from the reduction of the fatty acid radicals contained in fatty material.

50 5. In the production of wetting and cleansing agents, the combined steps of converting the carboxyl groups of a fatty material to primary alcohol groups and then sulphating.

55 6. In the production of wetting and cleansing agents, the combined steps of reducing the esters of fatty and oily acids having more than 8 carbon atoms to the corresponding higher alcohols and thereafter sulphating the resulting alcohols.

60 7. In the production of wetting and cleansing agents, the combined steps of reducing the esters of fatty acids having more than 8 carbon atoms

to the corresponding higher alcohols by treatment with an alkali metal and a lower alcohol, and thereafter sulphating the resulting higher alcohols.

8. The process of manufacturing wetting and cleansing agents which comprises reducing a fatty material to form higher alcohols corresponding to the fatty acid radicals contained therein, sulphating said higher alcohols to form alkyl sulphuric acids and neutralizing with a base to yield water-soluble salts of said alkyl sulphuric acids. 80

9. A composition of matter having soap-like properties consisting essentially of sulphuric esters of aliphatic alcohols having more than 8 carbon atoms obtained from fatty material by eliminating carboxyl groups from the carboxyl containing constituents. 85

10. Sulphated mixture of primary alcohols obtained by conversion of fatty materials containing fatty acids including combined fatty acids having more than 8 carbon atoms in the chain. 90

11. A wetting and cleansing agent comprising a sulphonation product of an unsaturated alcohol obtained by reducing an unsaturated fatty material having more than 8 carbon atoms. 95

12. The process of producing wetting and cleansing agents composed of alcohol sulphate salts having more than 8 carbon atoms comprising producing alcohols from a fatty material containing fatty acid radicals of more than 8 carbon atoms, sulphating said alcohols at a temperature sufficiently low to produce principally sulphates and in the absence of organic solvents of said alcohols, and then neutralizing the reaction products to form the salts of the sulphated alcohols. 100

13. The process of producing alcohol sulphates having from 12 to 18 carbon atoms inclusive, comprising producing alcohols from a fatty material containing fatty acid radicals of the above mentioned number of carbon atoms, and sulphating said alcohols at a temperature sufficiently low to produce substantially only sulphates and in the absence of organic solvents of said alcohols. 105

14. The product produced by the process described in claim 12. 110

15. The product produced by the process described in claim 13. 115

16. Sulphuric ester of primary stearyl alcohol. 120

17. A composition of matter having soap-like properties consisting essentially of sulphuric esters of normal primary aliphatic alcohols having from 12 to 18 carbon atoms inclusive, obtained from fatty material by eliminating carboxyl groups from the carboxyl containing constituents. 125

18. A soap-like material comprising essentially salts of acids of the group consisting of alkyl sulphuric acids and alkyl sulphononic acids derived from primary alcohols resulting from the reduction of the fatty acid radicals contained in fatty material. 130

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