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# UNITED STATES PATENT OFFICE

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## DETERGENT AND METHOD OF MAKING IT

Emil E. Dreger, Summit, N. J., and John Ross, New York, N. Y., assignors to Colgate-Palmolive-Peet Company, Jersey City, N. J., a corporation of Delaware

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18 Claims. (Cl. 260—459)

This invention relates to a new process for producing materials adapted to function as wetting agents, detergents or the like and to the materials themselves. More particularly, the invention relates to the utilization of short chain fatty acids, which are not ordinarily satisfactory for the preparation of detergents, wetting agents, and the like, for the production of materials which will function efficiently for these purposes.

The fatty oils that are commonly used in the production of detergent materials, almost invariably contain an appreciable percentage of fatty acid esters, the fatty acids of which contain less than 12 carbon atoms. The sodium salts of these fatty acids are of little or no value and if they are left in the mixture along with the salts of the higher fatty acids, the result is simply a corresponding amount of inactive or inefficient material in the final product. This fact has been recognized and in some instances these lower fatty acids have been removed to make the final product more effective.

The removal of such fatty acids, however, reduces the quantity of the final detergent product that can be produced from a given amount of fatty oil and yields, as a by-product, considerable quantities of these lower fatty acids. For example, about 21% of the fatty acids in cocoanut oil contain less than 12 carbon atoms, and about 13% of the acids in palm kernel oil also contain less than 12 carbon atoms.

According to the present process these fatty acids, containing more than 1 and less than 12 carbon atoms and which are almost entirely of the straight chain or normal variety, are reacted in such a way as to form useful, efficient detergents, wetting agents, or the like. Preferably, the fatty acids that are used according to the present process are straight chain fatty acids and have at least six and not over eleven carbon atoms.

Briefly, the process of the present invention is accomplished by converting these fatty acids into ketones, usually straight chain ketones since the fatty acids used are generally straight chain fatty acids; thereafter hydrogenating the ketones to form secondary alcohols; and finally sulphating the alcohols to produce secondary alcohol sulphuric acid esters. The acid esters may then be neutralized with lime, ammonia, alkali metal hydroxides or carbonates before use.

The fatty acids may be converted into ketones by any of the known methods, for example, by heating the calcium salts of the fatty acids, or by passing the fatty acids in vapor state and diluted with inert gas, over a catalyst, such as thoria, at an elevated temperature. The ketones thus formed may be freed from any unconverted fatty acid by washing them with a hot dilute solution of caustic soda and dried.

The hydrogenation of the ketones may be effected by the action of any of the common reducing or hydrogenating agents, such as nascent hydrogen, or hydrogen in the presence of a suitable catalyst. Satisfactory results have been achieved, for example, by performing the reduction in either ethyl or butyl alcohol solution with nascent hydrogen produced by the action of sodium metal on the alcohol. The reduction may also be effected by heating the ketones with sodium isopropylate.

The sulphation is performed by any of the common sulphating agents, such as sulphuric acid monohydrate (100%), oleum, chlor-sulphonic acid and alkyl sulphates. It has been found desirable in most instances to accomplish the sulphation in the presence of a dehydrating agent such as acetic anhydride, but this is not necessary and can be avoided if desired.

As an example of the application of the principles of the present invention to the production of detergents and the like from the lower fatty acids from cocoanut oil, several straight chain fatty acids were separately processed and several mixtures of straight chain fatty acids were also processed according to the principles of this invention. The fatty acid or mixture of fatty acids selected as the starting material was in each case passed over a thoria catalyst at a temperature of about 400° C. (350–450° C.), while admixed with approximately twice its volume of carbon dioxide. The ketones formed were washed with hot 5% caustic soda solution to remove unchanged acids, and dried.

The ketones obtained were next hydrogenated by dissolving the ketones in approximately twice their volume of ethyl alcohol, and adding a quantity of metallic sodium equal in weight to about 30% of that of the ketone. Although this method is operative it will at once be apparent that it is not well adapted for commercial use and hence it is contemplated that other methods of hydrogenation may be substituted therefor. For example, any of the ketones mentioned may be reduced to a secondary alcohol by treating in an autoclave in the presence of an activated

nickel catalyst with hydrogen gas under 2 atmospheres of pressure at about 150° C.

The secondary alcohols so produced were next converted into the corresponding sulphates by mixing equal parts by weight of the alcohol and acetic anhydride and stirring the mixture with external cooling, while slowly adding a weight of sulphuric acid (100%) equal to the weight of the alcohol taken. It was found that the reaction when conducted at a temperature between −20° to +35° C., was generally complete after about two hours stirring. At this point the mixture was poured into several times its volume of ice and water and extracted with butyl alcohol. The butyl alcohol extract contained the acid alkyl sulphate, some acetic acid and some water. The extract was neutralized by adding solid sodium bicarbonate with external cooling and the aqueous layer containing sodium acetate was separated leaving the sodium carbinol sulphate in the butyl alcohol. The butyl alcohol was then distilled off by passing steam through the butyl alcohol solution. This resulted in the formation of a concentrated aqueous solution of the sodium carbinol sulphate.

The above procedure was applied to caproic acid, caprylic acid and capric acid as well as to mixtures of capric and caprylic acids and of all three acids. The individual acids yielded di n-amyl carbinol sulphate salt, di n-heptyl carbinol sulphate salt, and di n-nonyl carbinol sulphate salt respectively. The mixture of caprylic and capric acid gave a mixture of di n-nonyl carbinol sulphate salt, di n-heptyl carbinol sulphate salt and n-heptyl n-nonyl carbinol sulphate salt. The mixture of all three acids produced in addition to the others n-amyl n-heptyl carbinol sulphate salt and n-amyl n-nonyl carbinol sulphate salt.

The relative wetting and foaming properties of solutions of some of the compounds are compared below, showing the outstanding and unusual efficiency of di n-heptyl carbinol sulphate sodium salt in these respects.

| Material | Foam cc. | | Wetting time | | |
|---|---|---|---|---|---|
| | 1% soln. | 0.5% in hard water 500 p. p. m. | 1.0% | 0.25% | 0.1% |
| Di n-heptyl carbinol sulphate sodium salt $C_{15}H_{31}O\ SO_2Na$ | 500 | 60 | 1 | 2 | 10 |
| n-Heptyl n-nonyl carbinol sulphate sodium salt $C_{17}H_{35}O\ SO_3Na$ | 400 | 20 | 2 | 9 | ------- |
| Di n-nonyl carbinol sulphate sodium salt $C_{19}H_{39}O\ SO_3Na$ | 275 | 10 | 9 | 50 | ------- |
| Mixed sodium salts of carbinol sulphates from mixtures of $C_6, C_8 C_{10}$ acids | 350 | 60 | 2 | ------- | 17 |

The foaming test was conducted by placing 50 cc. of the particular material in a 500 cc. stoppered graduated cylinder at room temperature and shaking the container 20 times in a vertical plane. The volume of the foam was read after allowing the container to stand two minutes.

The wetting test was conducted by comparing the time required by the various solutions to wet a one inch square of unused canvas drill. By placing 100 cc. of the solution to be tested in a beaker, the time required to wet the square of cloth dropped upon the surface of the solution can be readily measured with a stop watch. In most cases the cloth will sink to the bottom as soon as it is thoroughly wet.

Generally the secondary alcohol sulphates prepared by the process should contain at least 11 carbon atoms to be satisfactory as emulsifying and deterging agents. That is, if a single acid is used to prepare the secondary alcohol it should contain at least 6 carbon atoms and if a mixture of acids is used, the sum of the carbons in their chains should be at least equal to 12 carbon atoms. For example, n-butyric acid (4) and n-caprylic acid (8) will yield along with other sulphates, n-propyl n-heptyl carbinol sulphate salt which has 11 carbon atoms in the compound.

Although the preferred compounds are prepared from the straight chain fatty acids containing not less than 6 and not more than 11 carbon atoms, the process is adapted to the use of any straight or branch chain aliphatic monocarboxylic acids other than formic acid, whether derived from fatty oils or from any other source such as the oxidation of petroleum, alcohols and aldehydes, de-esterification of oils, fats and waxes and by organic synthesis.

Mixtures of lauric and n-butyric and of lauric and isobutyric acids were converted into ketones and the pure n-propyl undecyl ketone and isopropyl undecyl ketone obtained by fractionation. These were reduced to the respective carbinols which were converted into acid sulphates and neutralized.

The following comparison of the wetting and foaming properties of these two isomeric compounds discloses the marked superiority of the straight chain compound as a wetting agent.

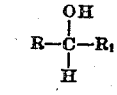
| Material | Foam cc. | | Wetting time | |
|---|---|---|---|---|
| | 1% soln. | 0.5% in hard water 500 P. P. M. | 1.0% | 0.25% |
| Isopropyl undecyl carbinol sulphate sodium salt $C_{15}H_{31}\ OSO_2Na$ | 325 | 115 | 13 | 73 |
| n-Propyl undecyl carbinol sulphate sodium salt $C_{15}H_{31}\ OSO_2Na$ | 300 | 100 | 2 | 22 |

The present invention is not to be restricted to any specific proportions or manner of procedure beyond the limitation of the appended claims.

We claim:

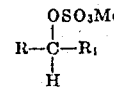
1. Dialkyl carbinol sulphates containing at least fifteen and not more than twenty-one carbon atoms, one alkyl chain being a straight chain containing at least five carbon atoms and the other alkyl chain being a straight chain containing at least three carbon atoms.

2. A process comprising sulphating a product of the general formula



containing at least fifteen and not more than twenty-one carbon atoms wherein R represents a straight chain alkyl group containing at least five carbon atoms and $R_1$ is a straight chain alkyl group containing at least three carbon atoms, by subjecting the same to a sulphating agent.

3. A sulphation product of the following general formula



containing at least fifteen and not more than twenty-one carbon atoms wherein R represents a straight chain alkyl group containing at least five carbon atoms, $R_1$ is a straight chain alkyl group containing at least three carbon atoms and Me is a radical of the group consisting of alkali metals, alkaline earth metals and ammonium.

4. A salt of a sulphated carbinol having at least two straight chain alkyl groups attached to the carbon atom of the carbinol group, one of which contains at least five carbon atoms and another containing at least three carbon atoms, there being at least fifteen but not more than twenty-one carbon atoms in all in said sulphated carbinol.

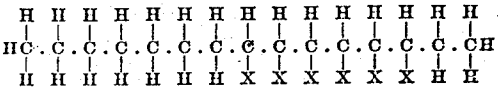
5. A process for preparing straight chain secondary alcohol sulphates from fatty acids which comprises reacting together fatty acids containing at least two carbon atoms to form at least one ketone containing at least eleven but not more than twenty-one carbon atoms and having the alkyl chains of two fatty acid molecules attached to a carbonyl group, reducing the ketone to a secondary alcohol, and sulphating the secondary alcohol.

6. A process for preparing secondary alcohol sulphate salt which comprises reacting an aliphatic carboxylic acid containing at least four and not more than twelve carbon atoms with an aliphatic carboxylic acid containing at least four and not more than twelve carbon atoms, the sum of the carbon atoms in the two acids being at least twelve but not more than twenty-two carbon atoms, to form a ketone containing at least eleven and not more than twenty-one carbon atoms, reducing said ketone with hydrogen in the presence of a metal catalyst to form a secondary alcohol, sulphating the secondary alcohol and neutralizing to form a salt of a secondary aliphatic alcohol acid sulphate.

7. A process for the manufacture of sulphates of secondary aliphatic alcohols which comprises converting a mixture of aliphatic monocarboxylic acids containing from 6 to 11 carbon atoms into a mixture of ketones containing from 11 to 21 carbon atoms by a catalytic decarboxylation process, reducing said mixture of ketones to a mixture of secondary aliphatic alcohols containing from 11 to 21 carbon atoms, and sulfating said mixture of secondary aliphatic alcohols.

8. A normal, secondary, pentadecyl sulphate.

9. A normal, secondary, pentadecyl sulphate having the general formula:



wherein one of the X's represents a sulphate group and all of the other X's stand for hydrogen.

10. A normal pentadecyl-8 sulphate.

11. An alkali metal salt of a normal, secondary pentadecyl sulphate.

12. A process of preparing an alkali metal salt of a normal, secondary, pentadecyl sulphate which comprises reacting a normal, secondary pentadecanol with chlorosulphonic acid in an inert, anhydrous, organic solvent and neutralizing the sulphated pentadecanol with an alkali metal hydroxide.

13. Normal sodium pentadecyl-8 sulphate.

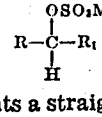
14. A process of making sodium pentadecyl-8 sulphate which comprises reacting pentadecanol-8 with chloro-sulphonic acid in an anhydrous organic solvent and neutralizing the sulphated pentadecanol-8 with sodium hydroxide.

15. A normal pentadecyl-4 sulphate.

16. Normal sodium pentadecyl-4 sulphate.

17. A normal pentadecyl-6 sulphate.

18. A mixture of sulphate esters of a plurality of straight chain secondary alcohols derived from a mixture of straight chain fatty acids, each of the esters of the mixture containing from eleven to twenty-one carbon atoms and having the general formula:



wherein R represents a straight chain alkyl group containing at least five carbon atoms, $R_1$ is a straight chain alkyl group containing at least three carbon atoms, and M is a cation.

EMIL E. DREGER.
JOHN ROSS.

CERTIFICATE OF CORRECTION.

Patent No. 2,321,020. June 8, 1943.

EMIL E. DREGER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 63, in the table, after "$C_8$" insert a comma; page 3, first column, line 32, claim 6, for "salt" read --salts--; and second column, line 17, claim 11, after the word "secondary" insert a comma; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of August, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.