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UNITED STATES PATENT OFFICE

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SULPHONATED HIGHER UNSATURATED CARBOXYLIC ESTERS OF POLYHYDROXY SUBSTANCES

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No Drawing. Application November 16, 1929, Serial No. 407,796

15 Claims. (Cl. 260—100)

My invention relates to a new class of chemical products and processes for making same. These substances have many advantages in the arts and many uses, which will be described later.

The materials I have discovered are fatty compounds with an oleaginous radical or group and with a sulphuric acid radical or radicals associated with it. My products are solid at ordinary temperatures and it is this property which, among others, distinguishes them from and endows them with important advantages over the "sulphonated" oils of commerce known heretofore.

Another departure which I make from the art of "sulphonation" as practiced heretofore is that the fatty material which I subject to the action of the sulphuric acid, chlorsulphonic acid or other "sulphonating" agent, is generally speaking relatively less unsaturated than the fatty oils used heretofore. The proportion of carbon to carbon double bonds per unit weight of material is relatively less than in the fatty oils used heretofore. Furthermore, as a consequence of this, my "sulphonated" products, may be prepared, if desired, to contain relatively smaller proportions of combined sulphuric acid than are present in the "sulphonated" oils made heretofore.

Throughout this application I use the term "sulphonation" primarily to designate the addition of sulphuric acid or its equivalents to a carbon to carbon double bond.

In a co-pending application, Serial No. 475,622, filed August 15, 1930, now Patent No. 1,917,250 I have described some of the methods I have used in the manufacture of such substances and their use in connection with the reduction of spattering in oleomargarine and like products during frying.

In the present specification I describe more fully the nature of these substances, various methods for their manufacture and point out their uses in the arts.

In the art known heretofore as the "sulphonation" of oils, oils which are liquid at ordinary temperatures such as olive oil or castor oil, were treated with sulphuric acid to produce materials which are liquid at ordinary temperatures, in which the sulphuric acid radical is added to a double bond producing acid sulphates insoluble in water, together with a not inconsiderable proportion of by-products such as free fatty acids.

In order to make them water soluble, these products are neutralized with alkali such as sodium ammonium, potassium hydroxide, carbonate or bicarbonate or the like or other alkaline agents.

Unsaturated liquid fatty acid such as oleic acid or fatty acids of castor oil, which are liquid at ordinary temperatures, were also "sulphonated" in the same manner, producing substances which are insoluble in water but which become water soluble after being neutralized with an alkali.

An object of my present invention is to produce derivatives of carboxylic esters which contain a hydrophylic radical such as a sulphate group and which are solid at ordinary temperatures. They also have certain distinct physico-chemical properties in that they are substantially insoluble in water but are colloidally dispersible therein. They also have the property of imbibing large amounts of water to an extent up to three to four times their own weight.

An example of one way in which my invention may be carried out is as follows: 100 pounds of oleo stearine, of the commercial kind obtainable from packing houses, are treated with 200 pounds of concentrated sulphuric acid, (sp. g. 1.84), preferably controlling the temperature so that it does not rise substantially above 38 or 40° C., by macerating, kneading or grinding the sulphuric acid with the oleo stearine and allowing the mixture to stand for a sufficient time to allow the reaction to run to completion, generally from twelve to eighteen hours.

The mixture is then mixed with about 500 gallons of cold water by maceration for the purpose of dispersing same. Thirty pounds of common salt are then dissolved in this mixture which is then allowed to remain at rest. The sulphonated carboxylic esters, together with a proportion of other reaction by-products, come to the top in the form of small curdy particles.

This product is washed several times with water, followed by salting out as above, so as to eliminate the free, uncombined sulphuric acid.

The washing out of the free uncombined sulphuric acid may be facilitated by dispersing the "sulphonated" material in warm water, say at 60 to 70° C. This gives a fine milky emulsion. A proportion of salt is now dissolved in this emulsion, 1½% or more, and the "sulphonated" material floats to the surface and forms, in many cases, a clear fat layer. The brine is drawn off. The "sulphonated" material may now again be dispersed in warm water and the procedure repeated until the free, uncombined sulphuric acid has been sufficiently washed out.

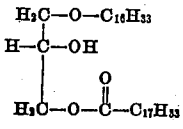
Finally the mixture is allowed to cool and the product is skimmed from the top. This product may contain imbibed water. More water may

be incorporated in it if it is desired to bring it into a pasty consistency.

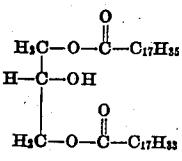
In place of oleo stearine, I can use other animal fats such as lard, or vegetable fats such as partially hydrogenated cottonseed oil, partially hydrogenated peanut oil, or cacaobutter or cocoanut oil, or, in fact, any of the glycerides which are usually solid at ordinary temperatures and which contain carbon to carbon double bonds capable of adding on sulphuric acid or other non-glyceridic esters with similar double bonds, but containing such double bonds in proportions smaller than present in the oils used heretofore for "sulphonation".

I do not wish to limit myself to the above method of manufacturing the solid "sulphonated" esters. I can use varying amounts of sulphuric acid, but the amount of sulphuric acid must be sufficient to produce the desired "sulphonation". In place of sulphuric acid of sp. g. 1.84, I can use fuming sulphuric acid, chlorsulphonic acid or other "sulphonating" agents.

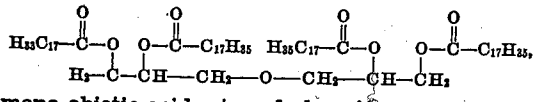
The application of my invention is by no means limited to triglycerides as I have obtained good products by treating other esters which are solid at ordinary temperatures and which contain carbon to carbon double bonds capable of adding on the elements of sulphuric acid. Examples of such esters are: cetyl glyceryl ether mono oleate



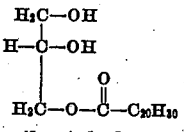
oleyl-stearyl glycerine



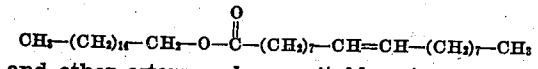
mono-oleyl-tri-stearyl diglycerol



mono abietic acid ester of glycerine



tri-stearyl castor oil cetyl olegate



and other esters such as suitable esters of glucose, sucrose, mannitol, sorbitol, diethylene glycol, etc.

I prepare these products by the same methods used in sulphonating oleo stearine. For example, 100 pounds of one of the esters described above are treated with 200 pounds of concentrated sulphuric acid (sp. g. 1.84), preferably controlling the temperature so that it does not rise substantially above 38 to 40° C., by macerating, kneading, or grinding the sulphuric acid with the product and allowing the mixture to stand for a sufficient time to allow the reaction to run to completion, generally from twelve to eighteen hours.

The mixture is then mixed with about 500 gallons of cold water by maceration for the purpose of dispersing same. Thirty pounds of common salt are then dissolved in this mixture which is then allowed to remain at rest. The sulphonated carboxylic esters, together with a proportion of other reaction by-products, come to the top in the form of small curdy particles.

This product is washed several times with water, followed by salting out as above, so as to eliminate the free, uncombined sulphuric acid.

The washing out of the free uncombined sulphuric acid may be facilitated by dispersing the "sulphonated" material in warm water, say at 60 to 70° C. This gives a fine milky emulsion. A proportion of salt is now dissolved in this emulsion, 1½% or more and the "sulphonated" material floats to the surface and forms, in many cases, a clear fatty layer. The brine is drawn off. The "sulphonated" material may now again be dispersed in warm water and the procedure repeated until the free, uncombined sulphuric acid has been sufficiently washed out.

Finally the mixture is allowed to cool and the product is skimmed from the top. This product may contain imbided water. More water may be incorporated in it if it is desired to bring it into a pasty consistency.

In sulphonating these products, I do not limit myself to the above described method. I may use various amounts of sulphuric acid, but the amount should be sufficient to "sulphonate" the product at the double bonds in order to produce the result desired. In place of sulphuric acid (sp. g. 1.84), I may use fuming sulphuric acid, chlorsulphonic acid or other "sulphonating" agents.

The term "sulphonation" is employed to define a mechanism wherein a sulphate group is attached at the carbon to carbon double bonds.

In general, my "sulphonated" products are superior to the "sulphonated" oils heretofore known in commerce principally by virtue of their property of being solid at ordinary temperatures. The uses of the "sulphonated" oils known heretofore are circumscribed by the fact that they are liquid at ordinary temperatures. This is a very important difference for it makes possible a wide field of usefulness for my products in the textile, paper, pharmaceutical, soap, cosmetic, dyeing, food and other industries as wetting, penetrating, detergent, foaming, lubricating agents, etc.

My "sulphonated" products may be used singly or as mixtures of several of my "sulphonated" products. Also, they may be compounded with soaps, "sulphonated" soaps, "sulphonated" oils, perfuming agents, dyes, medicating agents, abrasives or other materials, with which it may be desired to have them coact and such mixtures may be marketed as bars, sticks, crayons, pomades, powers, etc.

I am aware that wool fat, wool grease, or lanolin (which words are used almost synonymously), have been sulphonated to produce a water dispersible solid product. It is not my intention to claim substances of this kind as my invention is directed to sulphonated carboxylic esters of polyhydroxy compounds such as glycols, glycerine, and sugars. Many examples of these compounds are given in the preceding paragraphs. Although wool fat is called a fat, in a strict technical sense it is not a fat, but in some cases is composed almost entirely of cholesterol and cholesterol derivatives. The glycerides or fatty substances used in my invention, on the contrary, will be found to contain approximate-

ly only about one-half of one percent of cholesterol or less, and are, in most respects, true glycerides or fats.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A derivative of an unsaturated higher fatty acid ester of a sugar, the ester being solid at ordinary room temperatures, there being a sulphate group attached to a carbon at a double bond of the unsaturated fatty acid.

2. The method of forming a new chemical compound which comprises intimately mixing a higher unsaturated fatty acid ester of a sugar, which ester is solid at normal temperatures, with a sulphonating agent, allowing the mixture to stand until the sulphonating action is substantially completed, and finally neutralizing and washing the resulting compound until the excess sulphonating agent is removed.

3. A sulphonated derivative of a higher unsaturated aliphatic carboxylic acid ester of a water soluble carbohydrate, the ester being solid at room temperatures, the sulphate group being attached to carbon at a double bond of the acid radical.

4. A sulphonated derivative of a higher unsaturated aliphatic carboxylic acid ester of glucose, the ester being solid at room temperatures, the sulphate group being attached to carbon at a double bond of the acid radical.

5. A derivative of a higher unsaturated aliphatic carboxylic acid ester of a sugar, the ester being solid at ordinary room temperatures, and having a sulphate group attached to a carbon at a double bond of the unsaturated aliphatic carboxylic acid.

6. A derivative of an unsaturated higher organic carboxylic acid ester of a sugar, the ester being solid at ordinary room temperatures, and having a sulphate group attached to a carbon at a double bond of the unsaturated organic carboxylic acid.

7. The method of forming a new chemical compound which comprises intimately mixing a higher unsaturated aliphatic carboxylic acid ester of a sugar, which ester is solid at normal temperatures, with a sulphonating agent, allowing the mixture to stand until the sulphonating action is substantially completed, and finally neutralizing and washing the resulting compound until the excess sulphonating agent is removed.

8. The method of forming a new chemical compound which comprises intimately mixing a higher unsaturated organic carboxylic acid ester of a sugar, which ester is solid at normal temperatures, with a sulphonating agent, allowing the mixture to stand until the sulphonating action is substantially completed, and finally neutralizing and washing the resulting compound until the excess sulphonating agent is removed.

9. A sulphonated derivative of a higher unsaturated organic carboxylic acid ester of a water soluble carbohydrate, the ester being solid at room temperatures, the sulphate group being attached to carbon at a double bond of the acid radical.

10. A sulphonated derivative of a higher unsaturated fatty acid ester of a water soluble carbohydrate, the ester being solid at room temperatures, the sulphate group being attached to carbon at a double bond of the acid radical.

11. A sulphonated derivative of a higher unsaturated organic carboxylic acid ester of glucose, the ester being solid at room temperature, the sulphate group being attached to carbon at a double bond of the acid radical.

12. A sulphonated derivative of a higher unsaturated fatty acid ester of glucose, the ester being solid at room temperature, the sulphate group being attached to carbon at a double bond of the acid radical.

13. A sulphonated derivative of a higher unsaturated organic carboxylic acid ester of a polyhydroxy alcohol, the ester being solid at room temperatures, the carbon residue of said polyhydroxy substance containing more than three carbon atoms, the sulphate group being attached to carbon at a double bond of the acid radical.

14. A sulphonated derivative of a higher unsaturated aliphatic carboxylic acid ester of a polyhydroxy alcohol, the ester being solid at room temperatures, the carbon residue of said polyhydroxy substance containing more than three carbon atoms, the sulphate group being attached to carbon at a double bond of the acid radical.

15. A sulphonated derivative of a higher unsaturated fatty acid ester of a polyhydroxy alcohol, the ester being solid at room temperatures, the carbon residue of said polyhydroxy substance containing more than three carbon atoms, the sulphate group being attached to carbon at a double bond of the acid radical.

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