May 17, 1966 W. STEIN ETAL 3,251,868

SULFONATION OF SATURATED FATTY ACID
ESTERS OF POLYVALENT ALCOHOLS

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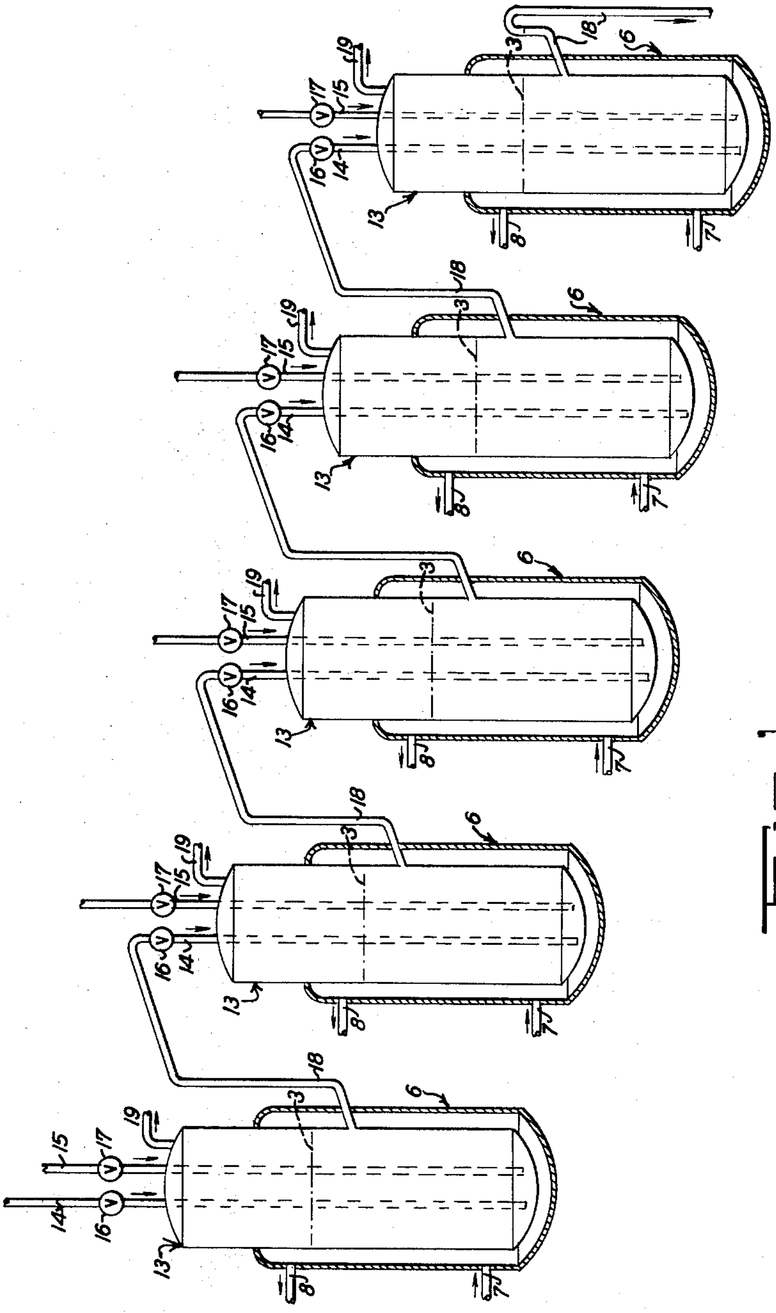

FIG. 1

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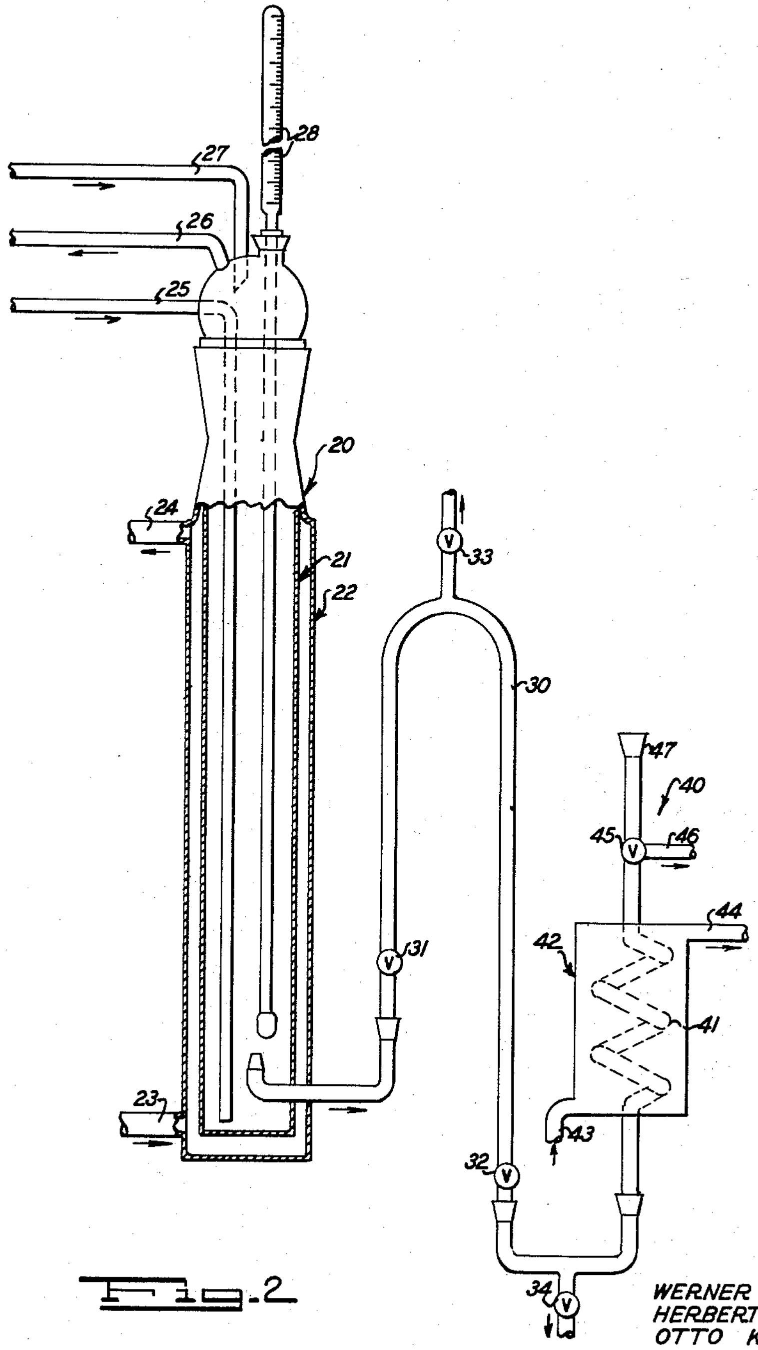

Fig. 2

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SULFONATION OF SATURATED FATTY ACID ESTERS OF POLYVALENT ALCOHOLS

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14 Claims. (260—400)

This invention relates to new and useful improvements in the sulfonation of fatty acid esters of polyvalent alcohols. The invention more particularly relates to an improved procedure for allowing a trouble-free sulfonation of esters of fatty acids and polyvalent alcohols, particularly fatty acid triglycerides into the corresponding alpha sulfonic acids using gaseous sulfur trioxide.

It is well known to convert the fatty acid esters of polyvalent alcohols, such as fatty acid triglycerides into the corresponding alpha sulfonic acids by a sulfonation reaction. For this purpose, liquid sulfur dioxide or sulfur dioxide dissolved in solvents has been used as the sulfonation agent. While the use of an excess quantity of gaseous sulfur trioxide, preferably diluted with inert gases, has proven practical as a sulfonation agent for other materials, such as fatty acids, the use of this sulfonation agent has not proven practical in connection with the fatty acid esters of polyvalent alcohols particularly of triglycerides as when sulfonating these materials with the sulfur trioxide gas, the viscosity of the reaction mixture increases to a point where further handling becomes difficult if not impossible and the gas stream containing the sulfonating agent produces enormous quantities of an uncontrollable foam which interferes with the reaction.

One object of this invention is the sulfonation of fatty acid esters of polyvalent alcohols, such as fatty acid triglycerides, using an excess of gaseous sulfur trioxide as the sulfonation agent, without the above-mentioned difficulties.

This and still further objects will become apparent from the following description read in conjunction with the drawings in which:

FIG. 1 diagrammatically shows an embodiment of a reaction vessel for effecting the sulfonation in accordance with the invention, and

FIG. 2 diagrammatically shows a further embodiment of an apparatus for effecting the sulfonation in accordance with the invention.

In accordance with the invention, it has now surprisingly been found that the prior art difficulties encountered in connection with the sulfonation of fatty acid esters of polyvalent alcohols using gaseous sulfur trioxide as the sulfonation agent and in particular the uncontrollable viscosity increase and foam formation may be avoided if the sulfonation is effected with the fatty acid esters of the polyvalent alcohols being an admixture with fatty acids or their derivatives, such as their esters with monovalent alcohols or their nitriles.

As the starting material for carrying out of the process in accordance with the invention, it is preferable to use natural triglycerides though synthetic triglycerides or synthetic esters of fatty acids with other polyvalent alcohols, such as for example glycols, pentaerythrite, mannite, sorbite, or the like may be used.

The fatty acid radicals present in both the fatty acid esters of polyvalent alcohols and fatty acids, fatty acid esters of monovalent alcohols or fatty acid nitriles, to be admixed therewith for the sulfonation in accordance with the invention, may be of any origin and should contain 6–28 and preferably 8–18 carbon atoms. These fatty acid radicals may, for example, come from the natural fats of plants, land-or-water-animals. Through selection of the starting fats, it is possible to extensively influence the properties of the sulfonates to be produced. Thus, from fats which preferably contain fatty acids with 10–14 carbon atoms per fatty acid radical, particularly from the fats of the lauric acid group, which are rich in fatty acid with 12 carbon atoms, products which are readily soluble at lower temperatures of, for example 20–45° C. are obtained. From other fats, which preferably contain fatty acids with 16–18 and more carbon atoms per fatty acid radical, for example from other plant fats than the above named, from tallow or from the whale- and fish-oils, there are obtained products which are particularly useful at temperatures within the range of 50–100° C.

The materials present in the mixture sulfonated in accordance with the invention should not contain further sulfatizable or sulfonatable groups, apart from alpha-position hydrogen atoms, such as for example double bonds or alcoholic hydroxyl groups.

The fatty acids, or their derivatives, i.e. the nitriles or esters with monovalent alcohols, may be any such material having fatty acid radicals as specified above. In connection, with the fatty acid esters of monovalent alcohols to be processed in accordance with the invention, these alcohols may be of primary and secondary nature and contain 1–20 carbons atoms in the molecule. Accordingly, for example, the esters of fatty acids with methyl- to nonyl-alcohols are applicable though it is also possible to use the fatty acid esters which contain radicals of still higher alcohols in the molecule as may be produced for example through reduction from the initially mentioned fatty acids or fatty acid mixtures or in other ways synthetically. Examples of easily accessible esters of fatty acids with higher fat-alcohols include the hydrogenation products of the oleylolate occurring in the sperm oil or the naturally occurring or synthetically produced wax-esters.

Many fats, particularly such of natural origin, and the fatty acids and their derivatives produced therefrom, often contain accompanying substances which in the sulfonation produce strongly colored decomposition products. Although it is possible to later bleach these decomposition products according to a process referred to hereinafter, it is advisable not to burden the sulfonation- and the bleaching-process by the presence of these accompanying substances and their decomposition product and to forthwith remove the same from the fats and/or the fatty acids or their derivatives produced therefrom. To such products, which cause upon the sulfonation, discoloration, belong, for example, unsaturated fatty acids or fatty acid derivatives. Therefore, the starting fats to be processed should be, as far as possible, extensively saturated, i.e. have iodine numbers below 5, and preferably below 2.

If fatty acids are added to the starting materials to be sulfonated in accordance with the invention, then distillates are preferably used as the starting material, which is also advisable in connection with the fatty acid derivatives sofar as these are distillable under the technical prerequisites in each case. If the starting materials are not initially purified by distillation, on account of a high boiling point or for other reasons may be distilled, as for example in triglycerides, then it is advisable to initially remove the impurities present in the starting material to be sulfonated by other conventional methods. Thus, for example in the case of the natural fats and particularly the natural triglycerides, albuminous substances and slimy substances (mucins), are separated by the deacidification and refining of the oils in a manner known per se.

In general, the benefits of addition of fatty acids and/or fatty acid derivatives, in accordance with the invention, are already noticeable if their quantity amounts to 5 weight percent of the entire starting material. However, larger quantities are preferred, as for example at least 10 and preferably 20–75 weight percent of fatty acid derivatives. In general, amounts of 85% fatty acid and/or fatty acid derivative will not be used.

Of the fatty acid derivatives, the esters of primary or secondary alcohols, containing 1–5 carbon atoms, have proved particularly suitable.

The fatty acids or other fatty acid derivatives, to be sulfonated in mixture with fatty acid esters of polyvalent alcohols, may have a chain-length-distribution of the fatty acid radicals which deviates from that of the esters of polyvalent alcohols, or which corresponds with it.

The sulfonation may be carried out continuously or discontinuously, by bringing together the sulfur-trioxide, diluted with an inert gas, with the starting material to be sulfonated. As inert gases, for example, air, nitrogen, carbonic acid, etc. may be used. The sulfur-trioxide content should amount to 2–40 volume percent, preferably 3–20 volume percent of the gas mixture.

The sulfonation agent quantities to be used per mol of fatty acid radical lie within the range of 1.1–1.8, preferably of 1.2–1.6 mol sulfur-trioxide, wherein with increasing length of the fatty acid-and alcohol-radical, greater sulfonation agent quantities are needed in order to attain high degrees of sulfonation.

The reaction sets in with practically serviceable velocities at about 30° C. and is appropriately carried out at gradually rising temperature. For the obtaining of high degrees of sulfonation, temperatures of 70–100° C., preferably of 75–95° C. and particularly of 80–90° C., are necessary. Since the quantity of the colored by-products, formed in the sulfonation, increases with rising temperature, it is advisable to hold the reaction mixture for as short a time as possible at the end temperature.

If one works in the interest of an extensive sulfonation at high temperatures, then the formation of brown-black colored decomposition products may not be avoided. There are, however, two sulfonation processes, with the aid of which it is possible to obtain a high degree of sulfonation with substantially decreased formation of the discolored decomposition products.

The one of these two processes is described in co-pending application Serial No. 194,840 filed on the same day herewith and consists in adding to the starting material in a first sulfonation step at temperatures of at most 70° C. not more than 65–90% of the sulfur-trioxide to be used, and then adding the residual sulfur-trioxide in a further sulfonation step or steps at higher temperatures. It is preferable to work with rising temperature, wherein the reaction starts in the first step at about 30° C. and preferably proceeds within the range of 40–65° C., and in the second step is carried out at temperatures of 75–95° C., preferably of 80–90° C. This process is particularly suitable for a continuous carrying-out, wherein one passes the starting material to be sulfonated through reaction zones, in which the temperature rises from zone to zone while the sulfur-trioxide is added in amounts calculated as required for the progressing reaction. These reaction zones may have the form of reaction vessels connected behind one another, in which an inert gas stream, containing sulfur-trioxide, is introduced into the reaction mixture and from which the sulfur-trioxide-free and/or sulfur-trioxide-poor inert gas stream is drawn off.

The second one of these two processes is described in co-pending application Serial No. 194,786 filed the same day herewith. According to this process, the sulfur-trioxide necessary for the sulfonation is dissolved in the starting materials to be sulfonated at temperatures which are not yet sufficient for a practically complete sulfonation, and only then the temperature is gradually brought to the height necessary for a complete sulfonation. The dissolving of the sulfur-trioxide appropriately occurs at temperatures within the range of 10–45 and preferably of 20–35° C., i.e. at temperatures at which the sulfonation does not proceed or proceeds comparatively slowly. Then, the temperature is gradually raised so that the sulfonation proceeds with technically serviceable speed, but not to completion, as for example to up to 70 and preferably up to 65° C. If there is obtained at these temperatures, up to 70° C., a degree of sulfonation of at least 50% and preferably of 60–80%, then the sulfonation is completed by raising the temperature to at most 100° C. and preferably 75–95 and most preferably 80–90° C.

The sulfonation products always contain excess quantities of sulfur-trioxide, which may be removed according to the process of co-pending application Serial No. 194,838, filed the same day herewith, now abandoned, by converting them with such substances, containing aliphatic hydroxyl groups, whose sulfatization products possess surface-active properties. These hydroxy hydrocarbon compounds contain as hydrophobic radical a hydrocarbon radical with 10–28 and preferably 12–18 carbon atoms, wherein in the case of alkyl-aromatic or cyclo-alkyl-aromatic radicals at least 8 of these carbon atoms must be of aliphatic or cyclo-aliphatic nature. Examples for such hydroxy hydrocarbon compounds are fat-alcohols or fatty acid alkylol amides or water-insoluble or water-soluble partial ethers or partial esters of fat alcohols, alkyl-phenols or fatty acids with polyvalent alcohols, wherein the partial ethers may be in the form of the addition products of ethylene oxide and/or propylene oxide to fat alcohols, alkyl phenols, acyl-phenols, fatty-acid amides or fatty acid alkylol amides or fatty acids.

If one converts the excess sulfur-trioxide present in the sulfonation products with these hydroxy hydrocarbon compounds forming surface-active substances, then it is possible to use in the sulfonation substantially larger quantities of sulfur-trioxide, for example, up to 2 or 3 mol sulfur-trioxide per mol fatty acid radical. This manner of working has the advantage that it is possible to obtain, with sulfonation temperatures below 70° C., high degrees of sulfonation.

In the conversion of sulfur-trioxide with fatty acids and/or their derivatives, the formation of colored impurities may not be entirely avoided even when using the above-mentioned processes. Therefore, it may be appropriate to bleach these products. Thus, it may be effected according to copending application Serial No. 194,998, filed the same day herewith, now U.S. Patent 3,159,657, using 0.2–6 weight percent, preferably 1–4 weight percent hydrogen peroxide, calculated as 100% product. If starting materials are processed which do not contain any impurities or accompanying substances, forming colored decomposition products in the sulfonation, then in general less than 4% and preferably less than 3% peroxide may be used. The hydrogen peroxide is charged preferably as 20–75 weight percent and most preferably as 30–50 weight percent-product. Furthermore, it is advisable, to thus choose the concentration of the hydrogen peroxide to be used in dependence on its quantity so that the sulfuric acid forming at the start of the bleaching process from free sulfur-trioxide and the water quantity introduced with the hydrogen-peroxide, is not more diluted than a 20% sulfuric-acid. Preferably this sulfuric acid is to represent, mathematically considered, a mixture of sulfur-trioxide and water with a sulfur-trioxide-content up to 95 weight percent and preferably up to 90–95 weight percent. The bleaching occurs at temperatures within the range of 20–100 and preferably of 40–80° C.

The bleaching of the sulfonation products may take place immediately subsequent to the sulfonation, or subsequent to the conversion of the excess sulfur-trioxide with hydroxy hydrocarbon compounds where provided. However, if the excess sulfonation agent is converted after the bleaching with added hydroxy hydrocarbon compounds, then it is advisable to adjust quantity and concentration of the hydrogen peroxide in dependence on the sulfur-trioxide-content of the reaction product so that the mixture of sulfur-trioxide and water, present in the reaction product (mathematically considered), corresponds at least to a 98% sulfuric acid. One may keep the water content so low that this mixture, mathematically considered, consists up to 95 weight percent and preferably of 80–90 weight percent of sulfur-trioxide.

A conversion of the excess sulfonation agent with the added hydroxy hydrocarbon compound, carried out after the bleaching, is above all most technically interesting, in the processing of sulfonation products containing fatty acids which are to be esterified with the added hydroxyl compound, or if one simultaneously wishes to re-esterify the sulfonated fatty acid esters.

The neutralization of the instant mixture of sulfonate and sulfuric acid ester with inorganic or organic bases takes place in the customary manner. If starting materials containing fatty acids have been sulfonated, then the preferably bleached sulfonic acids may be so neutralized that the sulfo-fatty-acids are present as mono-salts, which then are esterified in a manner known per se with added hydroxyl-compounds.

In the following examples, given by way of illustration and not limitation, the triglycerides processed have been treated for the removal of slime and subjected to deacidification and hardening. The iodine number of the hardened tallow amounts to 0, that of the hardened coconut oil amounts to 1. The fatty acid esters processed are practically saturated (iodine number not greater than 0.2) and have been purified through distillation.

In the case of the triglycerides, the mol-indications refer to the fatty acid radicals. In all cases the sulfonation products obtained at the end of the sulfonation were still well fluid and no difficulties whatsoever were encountered. In the sulfonation of triglycerides, however, without the additions in accordance with the invention, the viscosity of the reaction mixture rapidly increases and great quantities of a very stable foam form. Also a uniform working-in of the hydrogen peroxide into the sulfonation product cooled to temperatures below 50° C. is very difficult.

Example 1

Into a mixture of 61 g. hardened coconut-oil (0.25 mol) and 63 g. of the ethylester of a hardened palm-kernel-fatty-acid (0.25 mol) 52 g. sulfur-trioxide gas (0.65 mol), diluted with 20-fold volume-quantity of air, was introduced in the course of 60 minutes at 80° C. After the introduction, the mixture still remained standing for about 15 minutes at 89° C. The crude acid sulfonation product was bleached with 3% of its weight of H_2O_2 (as 40% aqueous solution) for 30 minutes at 60° C., and then neutralized with 5%-soda-lye. The degree of sulfonation of the product was 96.4%. A 5%-solution of the sulfonate, with reference to crude acid sulfonation product, showed in the Lovibond-Tintometer in a 4" cell, the following color values:

Yellow: 4.6; red: 0.4; blue: 0.1

Example 2

A mixture of 72 g. hydrogenated tallow (melting point 57.5° C.; 0.25 mol) and 62 g. of the ethylester of a hydrogenated palm-kernel-fatty acid (0.25 mol), mentioned in Example 1, was, as described in Example 1, sulfonated, bleached and neutralized. The degree of sulfonation of the product amounted to 98.5%; the Lovibond color values were:

Yellow: 1.4; red: 0.3; blue: 0.0

Example 3

A mixture of 83 g. hardened coconut-oil (0.375 mol) and 31 g. ethylester of a hardened palm-kernel-fatty-acid (0.125 mol) was, as described in Example 1, sulfonated, bleached, and neutralized. The degree of sulfonation of the product amounted to 79.1%; the color values measured in the Lovibond-Tintometer in a 4" cell were:

Yellow: 2.3; red: 0.6; blue: 0.4

Example 4

A mixture of 63 g. of the ethylester of a hardened palm-kernel-fatty-acid (0.25 mol), 37 g. of the ethylester of a hardened tallow fatty-acid (0.125 mol) and 28 g. of a hardened coconut-oil (0.125 mol) was, as described in Example 1, sulfonated, bleached and neutralized. The degree of sulfonation of the product amounted to 96.1%; the color values measured in the Lovibond-Tintometer in a 4" cell were:

Yellow: 1.0; red: 0.1; blue: 0.0

Example 5

A mixture of 60 g. of the methyl-ester of a hardened palm-kernel-fatty-acid (0.25 mol), 36 g. of the methylester of a hardened tallow-fatty-acid (0.125 mol) and 28 g. hardened coconut-oil (0.125 mol) was, as described in Example 1, sulfonated, bleached and neutralized. The degree of sulfonation of the product amounted to 97.4%, the color values measured in the Lovibond-Tintometer in a 4" cell were:

Yellow: 2.1; red: 0.5; blue 0.0

Example 6

For the carrying-out of the test here described, 5 of the vessels **13** shown in the drawing, were connected one after the other, in series. The starting material to be sulfonated is designated **3** and the lines **14** and **15** provided with the valves **16** and **17**, are for the introduction of the starting material to be sulfonated and the sulfur-trioxide-air mixture. **19** is an outlet for air, substantially free from sulfur-trioxide, and **18** an outlet for the reaction mixture. The lower part of the reaction vessel is surrounded by the heat jacket **6** with the heat exchange inlet **7** and outlet **8**.

As starting material, a mixture of 2500 g. ethylester of a hardened coconut-oil-acid and 2200 g. hardened coconut-oil was used.

At the start of the test, the first four reaction vessels were filled with ester and the heating adjusted so that the reaction mixture in the vessels had during the entire test the following temperatures, rising from vessel to vessel: 1st vessel, 50; second vessel, 60, 3rd vessel 70 ,4th vessel, 80, 5th vessel 80° C. Sulfur-trioxide, diluted with a 20-fold volume quantity of air, was blown into the first four vessels in such quantities that in the individual vessels, the following sulfur-trioxide-quantities (indicated in percent of the stoichiometrically necessary quantity for a quantitative sulfonation) were taken up 1st—52, 2nd—78, 3rd—104, 4th—130%. No sulfur trioxide was blown into the last vessel. After these quantities had been taken up, the processes were effected in continuous operation, and the first vessel was fed with 118 g. of the starting material per hour. Simultaneously, so much sulfur-trioxide-air-mixture was introduced into the first four reaction vessels that the above indicated sulfur-trioxide quantities had been supplied to the material leaving the individual vessels. No sulfur-trioxide, however, was blown into the last vessel as this vessel served for the after-reacting. The product running off from the apparatus was cooled and bleached with 2% of its weight H_2O_2 (as 40% aqueous-solution) for 2 hours at 55–60° C. and subsequently neutralized with 10% soda-lye. The degree of sulfonation of the product was 95%; the color values, measured in the Lovibond-Tintometer in a 4" cell were:

Yellow: 9.0; red: 2.0; blue: 0.0

Example 7

The sulfonation was effected in an apparatus according to FIG. 2. This device consists of an absorption vessel

20 and the heat exchange device 40, which are connected with one another through the line 30. The absorption-vessel 20 consists of an interior vessel 21, which is surrounded by a heating jacket 22 with feed-line 23 and discharge-line 24 for the heat exchange liquid. The starting material is introduced through the nozzle 27, while the sulfur-trioxide-inert gas-mixture is conducted through the line 25 under the surface of the starting material in the vessel 21. The inert-gas, practically free from sulfur trioxide, passes out at 26; the temperature is indicated on the thermometer 28, which also may be developed as thermo-regulating device, such as a thermostat which controls the flow of the heat exchange liquid.

At the bottom of the absorption-vessel, the starting material, containing sulfur-trioxide, is drawn-off through the line 30, which may be shut-off through the stop-cocks 31 and 32 as against the absorption vessel and/or the heat exchange device. The line 30 is bent upward in a U-shape and thus fulfills the function of a level-regulator. At the highest place, the deaerating-device 33 is mounted, while at the lowest point, shortly before the heat exchange device, is the discharge faucet 34.

The heat exchange device is developed as a coil 41 provided with the jacket 42 with the heat exchange agent-inlet 43 and outlet 44. The material passing out of the coil 41 may be carried off via the 3-way faucet 45, either through the nozzle 46, or conducted through the nozzle 47 into a further heat exchange device.

As starting material a mixture of 1332 g. (6 mol, referred to fatty acid-radicals) of a hardened coconut-oil (iodine number=0.5) and 1500 g. (6 mol) of the ethyl-ester of a hardened coconut-oil-acid.

(iodine number=0.3)

was used. Into about 1 mol (referred to fatty-acid-radicals) of this mixture, in the interior vessel 21 of the absorption-device 20, were blown-in in the course of about 2 hours at 30° C., 1.3 mol sulfur-trioxide, diluted with a 20-fold air quantity. After this quantity was dissolved, the sulfonation was continued as a continuous operation by adding per hour so much ester that the median time of stay of the ester in the absorption vessel amounted to 2 hours. The sulfur-trioxide was added continuously in a quantity of 1.3 mol per mol of fed fatty-acid-radicals. The three heat exchange coils, connected behind the absorption vessel, were held at temperatures of 60, 80 and 90° C. The time of stay in each coil amounted to about 20 minutes. The material had, upon passing out of the first reaction coil, a degree of sulfonation of about 65–70%.

The product passing out of the last reaction coil was cooled, then bleached with 2% of its weight of H_2O_2 (used as 40%-aqueous-solution) for 2 hours at 50–60° C., and neutralized with 10%-soda-lye. The degree of sulfonation of the product amounted to 94–95%. The Lovibond color values of the bleached product, measured as a 5%-solution of the sulfonate, with reference to crude acid sulfonation product, in a 4" cell, were:

Yellow: 18; red: 2.5; blue: 0.0

Example 8

Into a mixture of 53 g. (0.25 mol) of the ethylester of a hydrogenated palm-kernel-fatty acid (iodine number=0.3) and 56 g. (0.25 mol referred to fatty-acid-radicals) of a hydrogenated coconut-oil (iodine number=0.4), 52 g. (0.65 mol) sulfur-trioxide, diluted with 20-fold quantity of air, were introduced in the course of 15 minutes at temperatures of 30–40° C. The product thus obtained was heated in the course of 10 minutes to 70° C., where a degree of sulfonation of about 65% had been reached, and then the temperature was raised in the course of further 5 minutes to 80° C. after the product had been held for 45 minutes at this temperature, it was bleached for 8 hours at 30–40° C. with 2% of its weight of H_2O_2 (as 40%-aqueous-solution) and neutralized with 8%-soda-lye. The Lovibond color values of a 5% solution of the sulfonate, in reference to crude acid sulfonation product, amounted, measured in a 4" cell, to:

Yellow: 4.1; red: 0.7; blue: 0.0

While the invention has been described in detail with reference to certain specific embodiments, various changes that fall within the spirit of the invention will become apparent to the skilled artisan. The invention is, therefore, only intended to be limited by the appended claims or their equivalents wherein we have endeavored to claim all inherent novelty.

We claim:

1. In the process for the sulfonation of fatty acid esters of polyvalent alcohols which contain a substantially saturated unsubstituted fatty acid radical having from 6–28 carbon atoms, in which the ester is reacted with an excess of gaseous SO_3, the improvement which comprises effecting the sulfonation with the ester in admixture with about 20 to 85% by weight of an ester of a fatty acid having from 6–28 carbon atoms with a monovalent alcohol.

2. Improvement according to claim **1** in which said sulfonation is effected with said ester of the polyvalent alcohol in admixture with about 20–75% by weight of said ester of the monovalent alcohol.

3. Improvement according to claim **1** in which said ester of a monovalent alcohol is an ester of a lower monovalent alcohol.

4. Improvement according to claim **1** in which said ester of said polyvalent alcohol and said ester of said monovalent alcohol are purified materials having an iodine number below 5.

5. Improvement according to claim **1** in which said ester of said polyvalent alcohol and said ester of said monovalent alcohol are purified materials having an iodine number below 2.

6. Improvement according to claim **1** in which said sulfonation is effected in a multiple number of sulfonation steps with the starting mixture being initially contacted in the first sulfonation step at a temperature below 70° C. with from 60% to 90% of the sulfur dioxide quantity and in which the mixture is thereafter contacted in the subsequent sulfonation step at a temperature between about 75–95° C. with the remaining sulfur trioxide.

7. Improvement according to claim **1** in which the sulfonation is effected by initially dissolving the sulfur trioxide in the reaction mixture at a temperature between about 10–45° C., and thereafter increasing the temperature to a value not in excess of about 70° C. until a degree of sulfonation of at least 50% is reached, and thereafter further increasing the temperature to not in excess of 100° C. for completion of the sulfonation.

8. Improvement according to claim **1** in which said sulfur trioxide is used diluted with an inert gas stream.

9. Improvement according to claim **1** in which said sulfonation is effected at a temperature between about 30 and 100° C.

10. In the process for the sulfonation of fatty acid triglycerides containing a substantially saturated unsubstituted fatty acid radical having from 6–28 carbon atoms in which the triglyceride is reacted with an excess of a gaseous SO_3, the improvement which comprises effecting the sulfonation with the triglyceride in admixture with about 20 to 85% by weight of an ester of a fatty acid having from 6–28 carbon atoms with a monovalent alcohol.

11. Improvement according to claim **10** in which said ester of said fatty acid with said monovalent alcohol is present in amount of about 20–75% by weight.

12. In the process for the sulfonation of fatty acid triglycerides which contain a substantially saturated unsubstituted fatty acid radical having from 6–28 carbon atoms in which the triglyceride is reacted with an excess of gaseous SO_3, the improvement which comprises effecting the sulfonation with the triglyceride in admixture with about 20–85% by weight of a member selected from the group consisting of fatty acid methyl and fatty acid ethyl esters containing from 6–28 carbon atoms in the fatty acid radical.

13. Improvement according to claim **12** in which said group member is present in amount of about 20–75% by weight.

14. Improvement according to claim **13** in which said sulfonation is effected at a temperature between about 30 and 100° C. using sulfur trioxide diluted in an inert gas stream.

References Cited by the Examiner

UNITED STATES PATENTS

1,926,442	9/1933	Gunther et al. ------	260—400
2,691,040	10/1954	Bloch et al. ---------	260—400
2,878,271	3/1954	Little et al. ---------	260—400

FOREIGN PATENTS

617,347	8/1935	Germany.
288,126	4/1929	Great Britain.

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