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SULFOSUCCINATE ESTERS OF FATTY ACID MONO- AND DIGLYCERIDES

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9 Claims. (Cl. 117—139.5)

This invention relates to a new class of compounds which have outstanding characteristics as non-yellowing, softening agents for cotton and rayon textiles during hot finishing treatments and storage thereof. More particularly, the invention relates to a class of sulfosuccinic acid bis-esters of higher fatty acid glycerides possessing these desirable characteristics. The invention includes the novel softening agents, the methods of preparing the same, the method of softening textiles therewith, and the thereby improved textile products. In the course of their manufacture and finishing, cotton and rayon textiles are usually subjected to various heat treatments. Often, the textiles are coated or impregnated with fillers such as starch, gum tragacanth, gum ghatti, dextrines, and the like, in order to impart body to the cloth. Unfortunately, however, these treatments frequently result in the production of a relatively stiff fabric which is harsh-feeling and less desirable commercially than fabrics possessing a soft hand. Consequently, the industry has previously resorted to the use of several types of compounds for the softening of the finished fabric and, in the case of rayon textiles, for imparting thereto increased lubricity. Among the compounds hitherto employed by the art have been sulfonated hydrocarbons, waxes, stearates, and sulfated oils such as cottonseed oil, peanut oil, and similar oil products.

In view of the economics involved in textile manufacture, some of the most widely employed softening agents have been sulfated and/or sulfonated tallow, and sulfated and/or sulfonated mono- and diglycerides of tallow, cottonseed oil, coconut oil and other compounds containing the relatively long carbon chain of the higher fatty acids. However, it has been noted that the incorporation of even small amounts of these agents in cotton and rayon textiles has resulted in an undesirable yellowing of the fabric subsequent to the finishing thereof.

This is primarily due to the fact that the washed and/or sized fabrics are ordinarily dried at temperatures of about 250–400° F. and are then immediately rolled into bolts. The inner layers of the bolted cloth retain the heat for a period of several days during which time these sulfated or sulfonated softening agents, substantially all of which are relatively sensitive to heat, deteriorate sufficiently to cause serious yellowing of the treated fabric. Similarly, in the fabrication of garments from the treated textile materials, the cloth is frequently subjected to hot pressing operations at elevated temperatures which cause these softening agents to deteriorate. Therefore, although sulfated and sulfonated fatty acids and fatty acid glycerides are recognized as outstanding textile softening agents, their lack of heat stability has rendered them unfit for many textile finishing operations.

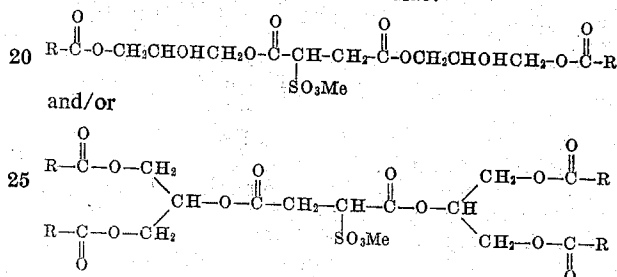
It has now been discovered, quite unexpectedly, that the members of a new class of bis-esters of sulfosuccinic acid and glycerides of higher fatty acids derived from particular sources possess outstanding textile softening proper-

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ties without any appreciable tendency to deteriorate under the influence of heat and bring about yellowing. In addition to these desirable qualities, this class of compounds has also been found to plasticize the starch sizes which are employed by the textile industry. Thus, the novel class of compounds of this invention provides the textile industry with a dual purpose agent which acts both as a non-yellowing, textile-softening compound and a plasticizer for starch-sized fabrics.

A further important advantage of the invention resides in the fact that all of the starting materials of the bis-esters of sulfosuccinic acid are readily available commercially at relatively low cost and, as pointed out above, this feature is extremely attractive to the manufacturers of textiles.

The novel class of non-yellowing textile softening agents of the present invention are believed to have the following general structural formulae:



wherein R is a higher fatty acid radical, preferably having from 12 to 18 carbon atoms and derivable from animal and/or vegetable oils having less than 15% by weight of polyunsaturated fatty acids therein; and Me is a salt-forming cation of the group consisting of alkali metals and ammonium.

The following animal and vegetable oils and fats are set forth as illustrative but not limitative of the type of oil or fat used as a selective source of the higher fatty acid glycerides: the vegetable oils, such as coconut oil; palm kernel oil; ouri-curi oil; ucuhiba oil, tea seed oil; olive oil; and palm oil; the animal fats such as lard, greases, Chinese tallow, mutton tallow and beef tallow; neats foot oil; etc.

It is to be particularly observed that these oleaginous materials do not possess any substantial amounts of hydroxy acids; that they contain less than about 15% by weight of polyunsaturated fatty acids; have relatively low iodine values (the quantity of iodine in mg. absorbed by 1 gm. of oil under normal conditions); and basically possess a non-drying nature.

Hydrogenated oils which do not contain any interfering hydroxy groups (such as in castor oil) may be used, provided the unsaturation of the fatty acids therein is reduced to below the above-mentioned 15% value and to correspondingly low iodine values. Such oils would include: hydrogenated cottonseed oil; hydrogenated corn oil; hydrogenated peanut oil; hydrogenated soya bean oil; hydrogenated sunflower seed oil; hydrogenated sesame oil; hydrogenated kapok oil; hydrogenated rapeseed oil; hydrogenated tung oil; etc.

Although these oils and fats contain fatty acids having various carbon chain lengths, the chain length of particular use within the concepts of the present invention lies in the range from about 12 to about 18 carbon atoms, with 16–18 being the preferred range.

It is, of course, to be understood that selected fatty acids, such as stearic acid, lying in the preferred range of carbon chain length, and possessing the properties and characteristics noted above, may also be used.

It is not essential that the sulfosuccinic acid bis-ester

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be the reaction product resulting from the use of 100% pure monoglycerides. A mixture of monoglycerides and diglycerides is normally commercially present and it has been found that a molar ratio of these two constituents within the range of about 50-95% of monoglyceride and about 50-5% of diglyceride is well adapted for application to the principles of the present invention. The presence of diglycerides in greater proportions than about 50%, however, undesirably decreases the water solubility characteristics of the compound and is to be avoided.

Briefly, the sulfosuccinic acid bis-esters are prepared by means of a three-step process. The monoglyceride (or the mixture of mono- and diglycerides) is prepared by reacting the selected animal or vegetable oil or fat with an excess of glycerol in the presence of a basic material such as an alkali or alkaline earth or heavy metal oxide or hydroxide, such as sodium hydroxide, calcium hydroxide or lead oxide. After the reaction to form the monoglyceride is complete, the basic catalyst is removed by precipitation as a fumarate salt.

In order to prevent the formation of an insoluble resin which is believed to be a cross-linked glycerol-maleic or fumaric ester, it is necessary to heat treat the monoglyceride in the presence of at least 10 mole percent of added fatty acid, e. g., stearic, palmitic, or oleic acid or their equivalents. A time of at least one hour and temperature of about 100–150° C. is desirable for this heat treatment.

The resulting heat-treated monoglyceride is then condensed with approximately one-half of an equimolar amount of maleic anhydride, or fumaric acid, or maleic acid to obtain the corresponding fumarate (maleate) bis-ester. This condensation product is then sulfonated by use of a bisulfite or metabisulfite containing a cationic salt-forming substituent, such as any of the alkali metals or ammonium. Preferably, the sulfonation is carried out by heating the bis-ester with an aqueous solution of alkali metal or ammonium bisulfite or metabisulfite whereby the corresponding salt is obtained directly.

Salts of other bases may be readily obtained by first acidifying an alcoholic solution of the alkali metal or ammonium salts whereby the free bis-ester of sulfosuccinic acid is obtained, filtering off the inorganic salt of the acid used and reacting the acid with the desired base. Although they are not ordinarily employed in textile finishing treatments, salts of the polyvalent metals such as calcium, barium, zinc, lead, cadmium, and the like may be prepared, if desired, by adding stoichiometric quantities of their oxides or hydroxides to the alcoholic sulfosuccinic acid ester solution followed by stirring until the salt formation is complete. Salts of organic bases such as methyl, ethyl, or butyl amine; guanylurea; guanidine; hydroxyethylguanidine; biguanide; ethanolamine; triethanolamine; or higher aliphatic amines; aromatic amines; and heterocyclic bases such as nicotine, pyridine, quinoline; and alkaloids may also be prepared by the same method as well as by direct sulfonation employing the sulfites and bisulfites of the organic bases.

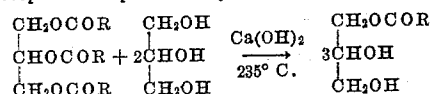
The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the present invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

EXAMPLE 1

The following is a description of a typical preparation of a sulfosuccinic acid bis-ester of tallow monoglyceride. The tallow used was a beef tallow, having an iodine value of 42.0, a saponification value of 198, and a solidifying point of 33° C. The beef tallow contained approximately 3.2% by weight of polyunsaturated fatty acids, primarily octadecadienoic acid.

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Step 1.—Preparation of tallow monoglyceride



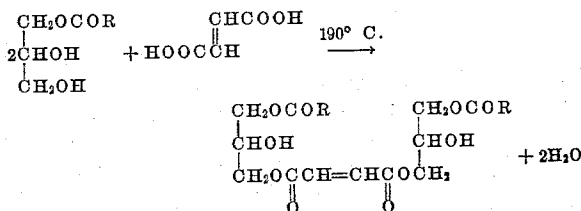
Where R is ca $C_{17}H_{35}$ —

Reactant	Weight	Pound Mole
1. Beef tallow	644 lbs.	0.75
2. Glycerol (98%)	169 lbs.	1.80
3. Calcium hydroxide	343 gms.	
4. Fumaric acid	648 gms.	

The first three materials were charged to a 100-gal., stainless-steel kettle. By means of liquid "Dowtherm" heating, the temperature of the reaction mixture was raised to and maintained at approximately 235° C., while nitrogen was passed into the kettle at a rate of from about 5 to about 6 liters per minute. When the methanol tolerance (the number of ml. of methanol per number of ml. of reaction mixture which produces an incipient cloudiness) had become constant at about 2½ to 3 hours at 235° C., the batch was cooled to 150° C.

The fumaric acid and 1% by weight of "Hyflo" were then added and, after 15 minutes agitation, the slurry was put through a 5-gal., stainless-steel, steam-jacketed, Sparkler filter. The filtrate was run into a 100-gal., stainless-steel pot and stirred for 24 hours in an oven at 80° C. The first 40 lbs. (the lower layer) was drawn off and set aside as this portion usually contained the bulk of the excess glycerol.

Step 2.—Preparation of the fumaric acid ester



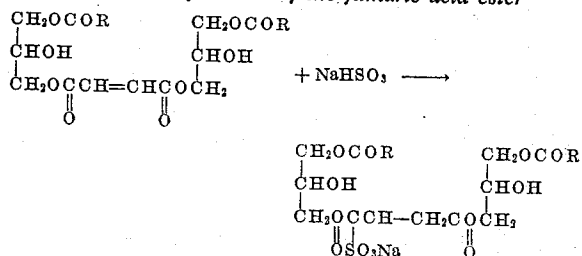
Reactant	Weight, lbs.	Pound Mole
1. Tallow monoglyceride	351	1.0
2. Stearic Acid (Hydrofol 405)	56.8	0.23
3. Fumaric acid	58.0	0.50
4. Xylene	62.0	

The monoglyceride resulting from Step 1 and the stearic acid were charged to a 100-gal., stainless-steel kettle equipped with liquid Dowtherm heating, propeller-type stirrer, nitrogen gas inlet tube, and a stainless-steel condenser fitted with a water trap. The charge was heated to and maintained at approximately 120° C. for two hours while passing nitrogen through the reaction mixture at the rate of about 4 liters per minute. The fumaric acid and xylene were then added and the temperature was raised to approximately 170° C. After 5 to 6 hours, all of the fumaric acid had reacted and the temperature had reached 190°–195° C. An amount of water usually somewhat in excess of the theoretical amount was collected in the trap. The xylene was stripped off at 160° C. and then finally at 160° C. at a reduced pressure of 30 mm. The batch was cooled to 120° C. and discharged into a 50-gal. receptacle.

The product was a moderately viscous brown liquid at 120° C. and a light tan waxy solid at room temperature. The acid number of several preparations varied between 10 and 2.

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Step 3.—Sulfonation of the fumaric acid ester



Reactant	Weight, lbs.	Pound Mole
1. Bis-tallow mono glyceride fumarate.....	438	
2. Sodium sulfite ¹	3.75	0.028
3. Sodium bisulfite.....	52.0	0.515
4. 2B Ethanol.....	115.0	
5. Water.....	50.0	

¹ The amount of sodium sulfite added is determined by the acid number of the charge. The amount of sodium bisulfite added is such as to give a total of 110% of theory. This total includes the NaHSO₃ derived from the Na₂SO₃.

The bis tallow monoglyceride fumarate, sodium sulfite, ethanol, and water were charged to a 200-gal., stainless-steel jacketed kettle equipped with a turbo-agitator and a stainless-steel condenser which could be used either for reflux or distillation. The charge was refluxed for approximately 15 minutes. At the end of this period, the sodium bisulfite was added and the batch was maintained at a reflux temperature of approximately 80° C. for about 12–19 hours. The sulfonation, as determined by an iodine titration of the excess bisulfite, was usually substantially complete and was in the range of about 90–100%. The batch was cooled to 60° C. and the calculated amount of hydrogen peroxide was added to oxidize the free bisulfite to bisulfate. The pH of the batch was then brought up to approximately 6.0–6.5 by the addition of either 10 or 20% sodium hydroxide solution. The mixture was concentrated to 80–85% solids to remove the ethanol, diluted with water to about 75% solids and discharged into 50-gal. containers. At 80° C. the product was a moderately viscous tan liquid which hardened to a stiff tan paste at room temperature.

EXAMPLE 2

The procedure set forth in Example 1 was repeated with mutton tallow being substituted for the beef tallow. The mutton tallow had an iodine value of 57.0, a saponification value of 196 and a solidifying point of 39° C. The mutton tallow contained approximately 5.5% by weight of polyunsaturated fatty acids, primarily octadecadienoic acid.

The reactions were substantially as described in Example 1 and the product was a moderately viscous tan liquid at elevated temperatures, hardening to a solid stiff tan paste at room temperature.

EXAMPLE 3

A sulfosuccinic acid bis-ester of coconut oil monoglyceride was prepared from a coconut oil having an iodine value of 7.2; a saponification value of 259; and a solidifying point of 16° C. The oil contained approximately 2.9% by weight of polyunsaturated fatty acids, primarily linoleic acid.

Step A.—Preparation of coconut oil monoglyceride

Coconut oil, 650 g., (1.0 mole, based on saponification number), glycerol, 221 g., (2.4 moles) and calcium oxide (3.0 g.) were placed in a two-liter, three-neck flask fitted with a stirrer, condenser, water trap, thermometer and nitrogen gas inlet tube. The temperature was rapidly raised to and maintained at 230–235° C. until the methanol tolerance of the reaction mixture had become constant. The temperature was then reduced to 150° C., and

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fumaric acid equivalent to the calcium oxide was added and, after a short interval of 15 minutes, the calcium fumarate thus precipitated was removed by filtration. The filtered product was allowed to stand at about 100° C. for approximately 3–6 hours and the glycerol which separated was removed. The final product was a pale tan, viscous liquid.

Step B.—Preparation of bis-coconut oil monoglyceride fumarate

Coconut oil monoglyceride, 556 g. (2.0 moles) and stearic acid, 112 g. (0.4 mole) were placed in a two-liter, three-neck flask, fitted as described in Step A, and heated to and maintained at 120° C. for two hours. At the end of this period, fumaric acid, 116 g. (1.0 mole), and 100 ml. xylene were added. The temperature was raised to and maintained at 175–180° C. until at least the theoretical amount of water of reaction had been obtained. The xylene was removed by distillation under reduced pressure. The product, acid number 105, was a tan viscous liquid.

Step C.—Sulfonation of the bis-coconut oil monoglyceride fumarate

Bis-coconut oil monoglyceride fumarate (from Step B) 748 g., together with 17.7 g. (0.14 mole) of Na₂SO₃, 125 g. of 2B-alcohol and 125 g. of water were placed in a three-liter, three-neck flask fitted with condenser and stirrer. Heating was by means of a steam bath. After 15 minutes of refluxing, 99.4 g. of NaHSO₃ (0.955 mole) was added and refluxing was continued until the sulfonation was at least 85% complete, as determined by titration of the unreacted sodium bisulfite present in the reaction mixture. The excess sodium bisulfite was oxidized to bisulfate with hydrogen peroxide and the pH of the reaction mixture was raised to 6–6.5 with sodium hydroxide solution. The alcohol was removed by distillation under reduced pressure and the percent solids was adjusted to 75% by addition of water. The product was a tan, viscous liquid.

EXAMPLE 4

The procedure set forth in Example 3 was repeated with olive oil being substituted for the coconut oil. The olive oil had an iodine value of 79; a saponification value of 194; a solidifying point of 1° C.; and contained approximately 13.6% by weight of polyunsaturated fatty acids, primarily linoleic acid.

The reactions were substantially as described in Example 3 and the product was a moderately viscous tan liquid at elevated temperatures, forming a soft paste at room temperature.

In employing the novel bis-esters of the invention in textile softening treatments, a dispersion of from about 0.5% to about 3% or more of the selected bis-ester is prepared in a water bath or, if the textile is to be sized at the same time, in an aqueous size bath. The textile material is thereafter impregnated in the bath to a wet pick-up of substantially 100% of the weight of fabric and then dried according to normal operating procedure. Ordinarily, where no sizing agent is employed it is unnecessary to have more than about 1% of the softening agent on the fabric in order to obtain the desired softness of hand in the product. On the other hand, where a sizing agent is used, it is sometimes necessary to increase the softening agent content to about 3% or more to obtain the desired improvement in softness of hand in the treated fabric.

The sulfosuccinic acid bis-esters of higher fatty acid glycerides of the present invention have been evaluated to determine their non-yellowing and softening properties and the following results have been obtained. The test samples were diluted from their 70–80% solid wax-like form to approximately 35% pastes and formed uniform white pastes with no difficulty. Several 1% solutions of various 35% pastes were padded onto 80 x 80 cotton

percale fabrics and compared to similar fabrics padded with a standard softener currently sold in large quantities on the open market. Hand evaluation for softness showed that the fabrics treated with the product of the present invention were consistently softer and possessed a fuller feel.

In order to test the non-yellowing characteristics of the present product, several pieces of rayon and cotton containing 1% finish were heated to and maintained at 95° C. for 72 hours in sealed jars. Reflectance measurements before and after heating showed considerably less yellowing, when compared to the yellowing obtained by the use of a standard non-yellowing softener currently sold in large quantities on the open market.

Although I have described several specific examples of my inventive concept, I consider the same not to be limited thereby nor to the specific substances mentioned therein, but to include various other compounds of equivalent constitution as set forth in the claims appended hereto. It is understood that any suitable changes, modifications and variations may be made without departing from the spirit and scope of the invention.

I claim:

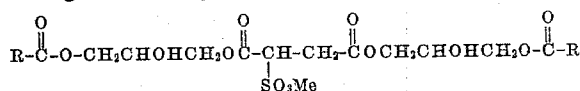
1. A bis-ester of sulfosuccinic acid with a substantially bi-molecular quantity of a member of the group consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof derived from a member of the group consisting of the animal and vegetable oils and fats containing less than 15% by weight of polyunsaturated fatty acids.

2. A bis-ester as defined in claim 1, wherein the higher fatty acid glyceride comprises a mixture of from about 50% to about 95% monoglyceride and from about 50% to about 5% diglyceride, said percentages being on a molar basis.

3. A bis-ester of sulfosuccinic acid with a substantially bi-molecular quantity of a member of the group consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof derived from tallow.

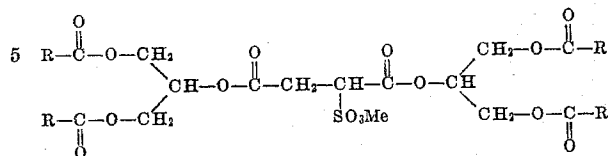
4. A bis-ester of sulfosuccinic acid with a substantially bi-molecular quantity of a stearic acid monoglyceride.

5. A sulfosuccinic bis-ester of a fatty acid glyceride having the following formula:



wherein R is a higher fatty acid radical derivable from a member of the group consisting of animal and vegetable oils and fats containing less than 15% by weight polyunsaturated fatty acids; and Me is a salt-forming cation of the group consisting of alkali metals and ammonium.

6. A sulfosuccinic bis-ester of a fatty acid glyceride having the following formula:



wherein R is a higher fatty acid radical derivable from a member of the group consisting of animal and vegetable oils and fats containing less than 15% by weight polyunsaturated fatty acids; and Me is a salt-forming cation of the group consisting of alkali metals and ammonium.

7. A method of preparing a sulfosuccinic acid bis-ester of a higher fatty acid glyceride which comprises esterifying a member of the group consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof derived from a member of the group consisting of animal and vegetable oils and fats containing less than 15% by weight polyunsaturated fatty acids and a member of the group consisting of maleic anhydride, fumaric acid and maleic acid, and then sulfonating the resulting product by reaction thereof with a water soluble bisulfite.

8. A method of treating textile materials which comprises impregnating the same with a softening and non-yellowing agent comprising a bis-ester of sulfosuccinic acid with a substantially bi-molecular quantity of a member of the group consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof derived from a member of the group consisting of the animal and vegetable oils and fats containing less than 15% by weight polyunsaturated fatty acids.

9. A non-yellowing textile material characterized by improved softness of hand comprising a textile material having distributed thereon a bis-ester of sulfosuccinic acid with a substantially bi-molecular quantity of a member of the group consisting of higher fatty acid monoglycerides, higher fatty acid diglycerides, and mixtures thereof derived from a member of the group consisting of the animal and vegetable oils and fats containing less than 15% by weight polyunsaturated fatty acids.

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