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TREATMENT OF FATTY ACID ESTERS AND PRODUCTION OF HIGH MOLECULAR WEIGHT ALCOHOLS THEREFROM

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This invention relates to the treatment of fatty acid esters and in particular is concerned with an improved process for treating fatty acid esters with mineral acids prior to their reduction to produce the derivative alcohols.

It has long been commercial practice to treat fatty acid esters of animal and vegetable origin with mineral acids, especially sulfuric acid, for the purposes of refinement. Briefly, such treatment involves heating the fats and oils to temperatures up to about 100° C. in the presence of sulfuric acid over a prolonged period of time. The mixture is then washed with water to remove the acid and the fat or oil is filtered to remove solid constituents. Still other treatments of fats and oils are known such as caustic treatment, high temperature heating, and the like. However, none of these prior art processes has proven satisfactory for the preparation of a product which is readily adaptable to reduction in an alkali metal-alcohol reducing process without the formation of stable emulsions in the hydrolysis step of this latter process.

The alkali metal-alcohol reducing process has likewise long been known and is commonly referred to as the Bouveault-Blanc process. This process involves treating fatty acid esters simultaneously with an alkali metal and a reducing alcohol, hydrolyzing the alcoholates so-formed and separating the alcohols therefrom. It is in the hydrolysis step of this process that the stable emulsions are encountered. These emulsions have necessitated longer residence times and considerable delay in production since the time required for breaking them was varied from about one-half hour to many hours in the absence of costly emulsion inhibitors. In order to obviate this problem, it has previously been proposed to reduce the ratio of solvent to the reducing alcohol in the hydrolysis step and also to add certain compounds as emulsion inhibitors such as phenolic compounds and other expensive inhibitors. However, these methods are either time-consuming, costly, or contaminate the products. Accordingly, a solution to this problem would be of particular benefit to the art and provide a material which is especially suitable for reduction by an alkali metal-reducing alcohol process.

It is an object of this invention to provide an improved process for treating fatty acid esters. A specific object of this invention is to treat fats and oils or fatty acid esters with a mineral acid in a manner which will result in a product of improved characteristics, especially adaptable for reduction to provide high molecular weight alcohols. A still further object of this invention is to provide a new and novel process for the production of high molecular weight alcohols. These and other objects will become apparent from the discussion hereinafter.

The above and other objects of this invention are accomplished by treating fatty acid esters dissolved in an inert organic liquid with a mineral acid in the presence of an alcohol. It is preferable to treat the esters under essentially reflux conditions—that is, within about 15° C. of the reflux temperature of the mixture, preferably for a period of time between about 0.5 and 180 minutes.

It is also preferable for best results to treat the fatty acid esters dissolved in at least 0.25 part of inert organic liquid per part of ester with a mineral acid under essentially reflux conditions in the presence of an alcohol in a proportion sufficient to provide an excess over that required to esterify the free fatty acids. Best results are achieved when the proportion of the alcohol is at least 20 percent of the chemical equivalent based upon the fatty acid ester in an alkali metal alcohol reduction process, and this quantity is still in excess of that required to esterify the free fatty acids. In a still more particular embodiment of this invention, fatty acid esters dissolved in at least 0.25 part by weight of inert organic liquid per part of said ester are treated with a mineral acid, especially sulfuric acid, in essentially catalytic quantities, and the treatment is conducted under essentially reflux conditions for a period of time between about 0.5 to 180 minutes in the presence of an alcohol in proportion which will provide an excess over the theoretical quantity required to esterify the free fatty acids, and this proportion is at least 20 percent of the chemical equivalent based upon the fatty acid ester in an alkali metal-alcohol reduction process and an excess of water over the theoretical based upon the free fatty acids is collected. It has been found that when treating fatty acid esters in this manner, the product thereby resulting when subjected to an alkali metal-alcohol reducing process does not form the stable emulsions in the hydrolysis step of this process. Thus, one aspect of this invention is the combination of treating fatty acid esters with a mineral acid as described and subjecting the so-treated esters to an alkali metal-alcohol reducing process. By our process the fatty acid esters are treated in a manner which will result in a product which, when subjected to an alkali metal-alcohol reducing process, will form an emulsion-free mixture in the hydrolysis step of this process. The term, "emulsion-free," is intended to connote a mixture having no emulsion, or if an emulsion does form, it will break within a period of about 10 minutes and preferably about 5 minutes. When a reduction process is to follow the treatment of the esters, it is preferable to employ a quantity of inert organic liquid and alcohol in the acid treat mixture which would be employed in the ester reduction process. By this method, the esters are treated and can be immediately reduced without additional operations. In still another embodiment of this invention, fatty acid esters are transesterified by reacting with an aliphatic alcohol in the presence of an alkaline alcoholysis catalyst. The newly formed esters dissolved in an inert organic liquid are treated with a mineral acid under essentially reflux conditions and in the presence of an alcohol, and the so-transesterified and treated esters are reduced by an alkali metal-reducing alcohol process to produce the corresponding alcohols.

The process of this invention as pointed out in its broadest aspects above has the particular advantage of providing a product of acid-treated fatty acid esters which when subsequently reduced by an alkali metal-alcohol reducing process do not result in stable emulsions in the hydrolysis step of this process. This feature is especially attractive to the industry inasmuch as it eliminates the costly and time-consuming emulsions which ordinarily must set for many hours or even days before the emulsions break or in some instances never do break. Further advantage is found when the proportions of the inert organic liquid and reducing alcohol in the acid treat step are essentially the same as those required for direct reduction. The presence of the reducing alcohol in the acid treat operation esterifies the free fatty acids, thus giving a higher yield of the fatty alcohol and decreasing the amount of soaps obtained. Further, the

alcohol re-esterifies any free fatty acids which might be formed. The process lends itself readily to a continuous operation without the necessity of drying, filtering, or other unit operations ordinarily required in other treatments of fatty acid esters or fats and oils of animal and vegetable origin.

To further demonstrate the process of this invention, reference is made to the following examples wherein all proportions are parts by weight unless otherwise specified.

EXAMPLE I

To a reactor equipped with a heating means, a means for agitation, and a reflux condenser having a water trap is added a mixture of 100 parts of tallow, having a saponification number of 195 and an acid number of 1.0, 100 parts of toluene, 23 parts of methylisobutylcarbinol, and 0.35 parts of concentrated sulfuric acid. The mixture was heated to the reflux temperature and maintained at that temperature for a period of about 60 minutes. From the vapors, water is condensed and collected in the water trap equivalent to the moisture content of the starting materials, and about 5 theories additional water based on esterification of free fatty acids. The toluene is returned to the reaction vessel. The product thus obtained, when subsequently reduced by an alkali metal-alcohol process, will be emulsion-free in the hydrolysis step of said reduction process.

EXAMPLE II

To a reactor equipped with a heating means, a means for agitation, and a reflux condenser equipped with a water trap was added a mixture of 100 parts of soy bean oil, having a saponification number of 199.5 and an acid number of 0.6, 100 parts of toluene, 76.4 parts of methylisobutylcarbinol, and 0.367 parts of concentrated sulfuric acid. The mixture was heated to the reflux temperature, about 110° C., and maintained under refluxing conditions for 60 minutes. During this period, 0.25 parts by weight of water was collected in the trap, about 0.2 parts of which were residual moisture. Without any further treatment, the mixture was then continuously fed to a dispersion, having an average particle size of 20 microns, of 34.5 parts of sodium in about 130 parts of toluene. The reaction mixture was maintained under a nitrogen atmosphere and at reflux conditions for a period of about 19 minutes. Upon initial feeding of the mixture to the sodium dispersion, hold-up of toluene was commenced and a total of 130 parts of toluene were removed by about 10 minutes after commencement of the feed to the dispersion. At the end of the 19-minute reaction period, the mixture was cooked for an additional 5 minutes. This reduction mixture was then added to 167 parts of hot water while continuously being agitated, and the temperature of the hydrolysis mixture rose without control. The temperature thus varied between about 60° and 100°. At the completion of the addition of the reduction mixture to the water, agitation was stopped. One-half minute after the agitation was stopped, the emulsion broke. The lower water layer containing caustic and glycerine was removed and the upper organic layer was fractionally distilled to separate the solvent and reducing alcohol from the product alcohols. The solvent and reducing alcohol were then recycled to the acid treat operation.

In contrast, when the same proportions of the above soy bean oil, solvent, alkali metal dispersion, and reducing alcohol were reacted essentially as described above, but without the pretreatment, an emulsion resulted in the hydrolysis step which did not break after standing for 180 minutes.

EXAMPLE III

The procedure was followed essentially the same as described in Example II, except that 0.36 parts of concentrated sulfuric acid was employed, the reflux time was 120 minutes, and the material treated was hydrogenated

tallow, having a saponification number of 205 and an acid number of 7.1. Exclusive of residual moisture, 0.49 parts of water was collected, representing about 2 theories based upon the free fatty acid content. The proportions of toluene and tallow were 100 parts each, and sufficient methylisobutylcarbinol was incorporated in the mixture to esterify the free fatty acids plus 5 percent excess of this alcohol over that required in the reduction step. After reduction using 5 percent excess sodium dispersed in toluene and hydrolysis, the emulsion which formed broke in 3 to 4 minutes. Another 100 parts of this same material was treated essentially the same as above, except that 0.734 parts of concentrated sulfuric acid was employed, the reflux time was 60 minutes, and the amount of water collected, excluding residual water, was 0.59 parts. Upon completion of the reduction and hydrolysis of the reduction mixture, the emulsion broke in 4 minutes. Thus, it can be seen that with a given raw material, the period of reflux is inversely proportional to the quantity of concentrated sulfuric acid to be employed.

In contrast to the above results, another portion of the hydrogenated tallow, which had not been treated with concentrated sulfuric acid as described, was reduced and an emulsion resulted during hydrolysis which did not break after standing for a period of 100 minutes.

EXAMPLE IV

Into a reaction vessel essentially the same as that described above was placed 100 parts of tallow having a saponification number of 195 and an acid number of 1.0 and 70 parts of toluene. Three-fourths part of sodium was added to 113 parts of methylisobutylcarbinol, and the resulting solution was added to the solution of tallow and toluene. The reaction mixture was then heated to the reflux temperature, about 110° C., and refluxed for 120 minutes. At the end of this time, the reaction mixture was neutralized with sulfuric acid, cooled, and two layers observed. Thus, the tallow glycerides were transesterified with methylisobutylcarbinol. The lower layer comprising essentially glycerol was removed and found to contain about 76 percent of the theoretical amount of glycerol. To the upper organic layer is added an additional 30 parts of toluene. Then about 0.35 parts of concentrated sulfuric acid is added to this mixture, and the mixture is heated to the refluxing temperature and refluxed for about 60 minutes. During this time, water which is formed is collected in the water trap. Thus, the methylisobutylcarbinol esters of the fatty acids of tallow have been acid treated. At the completion of this period, the reaction mixture is then fed to another similar reactor containing a previously prepared dispersion of 33.4 parts of sodium in 130 parts of toluene. This reduction reaction mixture is maintained under a nitrogen atmosphere and heated to reflux conditions. Upon starting the feed of the mixture to the sodium dispersion, hold-up of toluene is commenced and a total of 130 parts of toluene is removed within about 10 minutes after commencement of the feed. The reaction mixture is maintained under reflux conditions for about 19 minutes and is then cooked for an additional 5 minutes. This mixture is then added to 180 parts of hot water while continuously being agitated, and the temperature will rise so that the range is between about 60 and 100° C. At the completion of the addition of the reduction mixture to the water, agitation is stopped and a slight emulsion which is evident will break in less than 10 minutes.

To further demonstrate the process of this invention, reference is made to the following table wherein contrast is shown of the emulsion break time of various materials when reduced and hydrolyzed in the absence of and with treating according to our invention. In each instance, the original treat mixture contained the required amount of methylisobutylcarbinol to esterify the free fatty acids and to provide 5 percent excess of the theoreti-

cal quantity required to reduce the esters. A 1 to 1 solvent to ester ratio was employed.

Starting Material	Wt.	Conc'd H_2SO_4 Wt.	Reflux Time (Min.)	H_2O Collected (Wt.) [1]	Theoret. H_2O	Emulsion Break-time (Min.)
Hydrogenated tallow	100	0	0	0		110
Sap. No. 200	100	0.1	60	0.15	0.012	5
Acid No. 0.4	100	0.2	60	0.25	0.012	3-4
Edible Tallow	100	0	0	0		100
Sap. No. 195.0	100	0.2	60	0.1	0.032	10-11
Acid No. 1.0	100	0.3	60	0.1	0.032	3
Fancy Tallow	100	0	0	0		30
Sap. No. 190.7	100	0.4	60	0.59	0.11	1
Acid No. 3.4	100	0.2	60	0.39	0.11	2

[1] Moisture content of starting materials not included.

In examining the above table, it can readily be seen that in treating a given starting material with acid to reduce the emulsion break period, the period of reflux time is inversely proportional to the quantity of acid employed. Because of the variance in nature and analysis of the starting materials, as exemplified above with three grades of tallow, the quantity of acid to be employed and the reflux time is best determined experimentally on a small scale before conversion to a commercial operation. That is, a sample of the raw material is treated according to this invention with the acid in various quantities and under various reflux periods to determine that quantity of acid which for a given reflux period will result in a product which, upon reduction and hydrolysis, will form an emulsion-free mixture. However, in general, irrespective of the starting material to be employed, it is preferred here that between about 2 to 0.05 parts by weight of the concentrated mineral acid to 100 parts by weight of the fatty acid esters be employed and the treat time be between about 0.5 minutes and 180 minutes. Best results are obtained when the proportion of the mineral acid is between about 1.05 to 0.05 parts to 100 parts by weight of the fatty acid esters, and the reflux period is about 60 minutes.

We employ mineral acids in the treatment of the fatty acid esters. Generally speaking, any mineral acid can be employed, but the oxidizing mineral acids are preferred, especially sulfuric acid. Other mineral acids which can be employed are, for example, nitric, permanganic, chromic, and the like. It is also most preferable to employ the oxidizing mineral acids in their concentrated form, that is, above about 95 percent by weight. Lesser concentrations can be employed, however, these are not desirable in that appreciable quantities of water will be introduced which should be removed, especially when the treated fatty acid esters are to be reduced by an alkali metal-alcohol reducing process.

The organic liquids which we employ as solvents should be inert to the reactants, namely, the fatty acid esters, the treating acid, and the esterifying alcohol. If the treated fatty acid esters are to be later reduced, which is the preferred embodiment of this invention, the inert organic liquid should also be non-reactive with alkali metal and essentially immiscible with water. The inert organic liquids which we especially prefer are the hydrocarbons such as toluene, xylene, dihydronaphthalene, petroleum fractions, heavy alkylates, kerosene, benzene, the octanes, nonanes and decanes, mineral oil, tetralin, cumene, decalin, and the like. Another criterion of choice of solvent is that it have a boiling point approaching that of reaction conditions and preferably one which will form a water azeotrope. By employing these preferred solvents, water is removed from the reaction mixture which would hinder the treat and esterification of the free fatty acids. Still other solvents can be employed as, for example, alcohols, ethers, and the like, providing they are essentially inert to the particular reactants. The

proportion of inert organic liquid employed can be varied within wide limits. However, best results are achieved when at least 0.25 parts by weight of the liquid per part by weight of fatty acid ester is employed. Proportions below this limit are not satisfactory in that insufficient contact with the moisture is obtained, thus preventing efficient removal of this moisture from the reaction mixture during reflux and permitting reverse equilibrium of the esterification. When the treatment is to be followed by reduction which is the preferred embodiment of this invention, the solvent is generally employed in proportions between about 0.25 to 10 parts per part by weight of fatty acid ester. In most instances, proportions of the inert organic liquid above 1.3 parts per part of fatty acid ester are not required. Thus, good results are achieved when between about 0.25 to 1.3 parts by weight of solvent to 1 part by weight of fatty acid ester are employed.

The alcohols employed in the acid treat can be any primary, secondary, or tertiary alcohol, and preferably those which are liquids under the reaction conditions. The secondary alcohols are employed when the treatment is to be followed by reduction primarily due to their lesser reactivity with the alkali metal. Among such alcohols are, for example, propanol-2, butanol-2, pentanol-2, pentanol-3, 2-methylbutanol-3, methylisobutylcarbinol, cyclohexanol, cyclopentanol, phenylethyl carbinol, and the like. Still other secondary alcohols can be employed, the foregoing serving merely as illustrative examples. Likewise, the tertiary alcohols such as tertiary butyl, and tertiary amyl, can be used with good results. The primary alcohols can be used but have not been found to be as satisfactory as the secondary or tertiary alcohols. The proportion of the alcohol to be employed is preferably in excess of that required to esterify the free fatty acids. Best results are obtained when the proportion of alcohol is in excess of that required to esterify the free fatty acids and is at least 20 percent of the chemical equivalent of alcohol based upon the fatty acid esters. In the preferred embodiment wherein the treated esters are reduced, it is advantageous to employ sufficient alcohol to esterify the free fatty acids and provide an excess of about 5 percent over the quantity required in the reduction step. The incorporation of the requisite amounts of solvent and alcohol for reduction in the acid treatment provides a mixture suitable for direct reduction without the necessity of intermediate distillation, addition, or separation.

It should be pointed out that the incorporation of an alcohol in our treatment is primarily to esterify the free fatty acids. However, such esterification in the absence of the specific acid treatment of our process has no appreciable effect in the emulsion characteristics of the product when subsequently reduced. For example, runs were conducted in which simple esterification of the free fatty acid content of the raw material was obtained by reaction with a secondary alcohol in the presence of sulfuric acid as a catalyst. When the resulting material was reduced, no appreciable change in the breaking time of the emulsion which formed was exhibited. The emulsion break-time was again about 100 minutes, thus mere esterification of the free fatty acids does not eliminate this problem.

As noted, more than the theoretical quantity of water, excluding residual moisture of starting materials, over that obtained from esterification of the free fatty acids is collected. In general, the fatty acid esters are treated in a manner to collect between about 1.05 and 20 theories of water based upon the free fatty acid content. It is preferred here to remove between about 2 and 10 theories of water. Removal of such excess water during the treatment results in a substantial lowering of the emulsion break-time in a reduction process.

Our process is particularly adaptable to treating the fatty acid esters of tallow. Among such esters are the naturally occurring glycerides of tallow, hydrogenated

tallow, and tallow which has been transesterified with other alcohols than glycerol. In treating tallow, it has been found that best results are achieved when between about 0.75 and 0.2 parts by weight of mineral acid per 100 parts by weight of tallow are employed in the presence of about 1 part by weight of toluene per part by weight of tallow, at a reflux time of between about 40 and 120 minutes in the presence of at least 50 percent of the chemical equivalent of an alcohol based on the ester. It has been found that these conditions provide a product of tallow fatty acid esters which, when subsequently reduced, do not form an emulsion in the hydrolysis step which will not break within about 10 minutes.

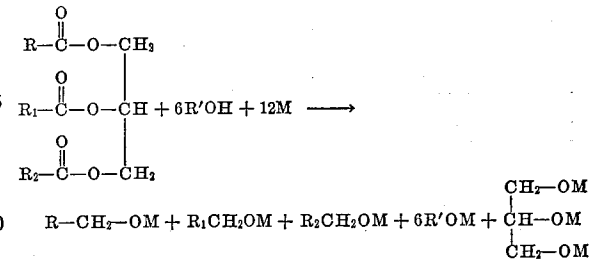
The process of this invention can be applied to numerous other fatty acid esters. Among such materials are babassu, coconut, castor, palm, sperm, peanut, carnauba, cashew nut, cotton seed, linseed, soybean, menhaden, and the like fats, oils, or waxes. Still other fats, oils, and waxes can be treated according to the process of this invention, the foregoing serving merely as illustrative examples. Likewise, the monoesters of these materials obtained by transesterification or other methods can be employed in the process of this invention. Similarly, hydrogenated or partially hydrogenated triglycerides or monoesters of fatty acids can be treated according to this process. In general, the esters of acids having between about 8 and 40 carbon atoms can be employed. Particular oils or esters which can be treated in this fashion are those which by prior art methods have resulted in stable emulsions in the hydrolysis step of an alkali metal-alcohol reducing process.

In some instances when treating the fatty acid esters with a mineral acid, there will be a tendency of the reaction mixture to foam. In order to obviate this difficulty, we prefer to employ a reaction vessel in which the upper portion contains a cooling coil or other foam-breaking means. The cooling coil knocks down the foam and prevents it from being entrained in the refluxing vapors. Other methods for eliminating the foam can be employed as, for example, defoaming agents and the like. It is also advantageous to provide efficient agitation to the reaction mixture. These and other modifications will be apparent.

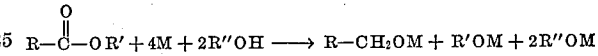
A particular embodiment of this invention is treating fatty acid esters with a mineral acid and then subjecting the so-treated fatty acid esters to an alkali metal-alcohol reducing process. This operation broadly consists of treating the fatty acid esters simultaneously with an alkali metal and reducing alcohol, hydrolyzing the resultant mixture, and separating the product alcohols therefrom. The alkali metal can be employed in either a solid or liquid form. In either event, it is preferred that the metal be utilized in the form of finely divided particles, and hence, alkali metal dispersions, especially sodium dispersions are particularly well suited for this process. The dispersion is a suspension of finely divided metal uniformly dispersed and suspended in an inert liquid, preferably a hydrocarbon. These dispersions are well known and are ordinarily prepared by vigorously agitating a mixture of sodium in a dispersion medium at a temperature above the melting point of sodium but below the boiling point of the dispersion medium. The dispersion medium can be any of those media which are commonly employed. It is preferred to employ as a dispersion medium inert organic liquids especially the hydrocarbons and especially the inert organic liquid which is employed in the acid treat operation. The concentration of sodium in such a dispersion most common is up to about 60 percent by weight. It is preferred here to employ a dispersion of about 50 percent by weight or less. The particle size of the sodium will vary from very minute particles up to about 50 microns in size. In a preferred embodiment, the average particle size should be below 20 microns. The preferred specifications of the alkali metal dispersion as presented above have been found to be more efficient in an alkali metal-alcohol reduction process.

The quantity of alkali metal and reducing alcohol employed in the reduction step can be varied within wide limits. In a preferred embodiment, these materials are used according to the theoretical quantity and up to about 5 percent in excess of that quantity as shown in the following equations, wherein Equation I describes the reduction of fatty acid esters comprising essentially triglycerides, and Equation II shows the reduction of fatty acid monoesters.

Equation I



Equation II



In both equations, R, R_1, and R_2 can be the same or different and are carbon chains having between about 8 and 40 carbon atoms; R' and R'' can be the same or different and are alkyl or cycloalkyl radicals of the alcohols mentioned previously; and M is an alkali metal.

When solvents are employed in conducting the reduction step of this process, they can be any solvent which is substantially unreactive with the particular reactants such as hydrocarbons, alcohols, ethers, and the like. Generally, it is preferred to use the same solvent which is employed in the acid treat or in the preparation of the alkali metal dispersion, as set forth previously. The use of a solvent is frequently desirable in order to maintain the fluidity of the reaction mixture. To achieve adequate fluidity, the proportion of solvent to ester can be as high as about 10 to 1 parts by weight. However, because of the pretreatment operation and other features of this invention, excessive quantities of solvent are not required. In fact, quantities less than about 1.3 parts by weight of solvent per part by weight of fatty acid ester are generally found to be sufficient. In a preferred embodiment, the solvent to ester ratio is maintained between about 0.25 and 1.3 to 1.

It has been found that when a combination of the acid treatment and reduction process is employed, the above limits in the reduction process provide the best results for the production of the high molecular weight alcohols. Thus, it is preferable to employ the same solvent and alcohol in each of these steps in their requisite amounts as pointed out above, taking into account variables such as free acid content, fluidity, excesses, and the like. It should, however, be understood that the solvent or alcohol in the acid treat need not be the same as the solvent or alcohol employed in the ester reduction. That is, different solvents or alcohols can be employed in each step and in some instances, particular advantage can be achieved although such variation in the materials has not been found necessary.

Another embodiment of this invention is to transesterify the fatty acid esters prior to conducting the actual reduction process. Such a procedure has been found to be beneficial in the case of triglycerides, inasmuch as the glycerine is more readily separated and recovered. Briefly, the transesterification comprises reacting a glyceryl ester of a fatty acid with an aliphatic alcohol in the presence of an alkaline alcoholysis catalyst and recovering the newly formed esters and glycerol therefrom. In some instances, it is desirable to conduct the transesterification in the presence of a solvent. In this instance, it is preferred to employ the same solvent as that

which is employed in the acid treat step. It is further preferred to react the glyceryl esters of the fatty acids with an aliphatic alcohol containing at least 2 carbon atoms in the presence of an alkaline alcoholysis catalyst and, when employed, in the presence of at least 20 percent, based upon the weight of the glyceryl ester used, of solvent. Preferred alcoholysis catalysts are the alkali metal hydroxides, alkali metal amides, alkali metal hydrides, and the like. Any alcohol can be employed as the esterifying alcohol, that is, primary, secondary, or tertiary alcohols, although the secondary alcohols, particularly methylisobutylcarbinol, are preferred here. The transesterification step can be conducted either prior to the acid treatment step or after the acid treatment and prior to the ester reduction stage. In the preferred embodiment, the transesterification is conducted prior to the acid treat, thus eliminating a neutralization step and providing more economical employment of the esterification catalyst and treating acid. In this operation, the resulting monoesters have also been found to be more readily adaptable to an ester reduction process, particularly when the secondary alcohols are employed as the transesterifying alcohol.

If the treated fatty acid esters are not to be employed in an ester reduction operation, it is preferable to neutralize the mineral acid in order to obviate the possibility of deterioration of the product by the acid. If the treated fatty acid esters are to be reduced, it is preferable that they be reduced as described above without intermittent storage. The treated fatty acid esters can be stored without neutralization or other similar operations, although storing for prolonged periods is not preferred.

As mentioned previously, the process of this invention finds particular utility in providing treated fatty acid esters which do not result in a stable emulsion when subsequently reduced by an alkali metal-reducing alcohol process. The treated fatty acid esters can also be used as such, as plasticizers, intermediates for other chemicals, additives to lubricants, paints and varnishes, and the like. When the treated fatty acid esters are reduced, the alcohols obtained thereby are particularly useful in the preparation of detergents, wetting agents, other chemicals, and the like. These and other uses will be apparent.

Having thus described our process, it is not intended that it be limited except as noted in the appended claims.

We claim:

1. A process which comprises heating crude esters of fatty acids having from 8 to 40 carbon atoms per molecule with a mineral acid under essentially reflux conditions in the presence of a monohydric alcohol and dissolved in an inert organic liquid selected from the group consisting of hydrocarbons, ethers, and excess alcohol, for a period sufficient to generate more than the theoretical quantity of water based upon esterification of the free fatty acids and the moisture content of the starting materials, and separating at least about 1.05 theories of said water from the reaction mixture during said heating.

2. A process which comprises heating for about 60 minutes crude esters of fatty acids having from 8 to 40 carbon atoms per molecule with sulfuric acid under essentially reflux conditions in the presence of a monohydric alcohol and with the ester dissolved in an inert hydrocarbon liquid, the proportion of the sulfuric acid being between about 1.0 to 0.05 part for every 100 parts by weight of the esters, and continually separating water from the reaction mixture as it is heated, to drive off any initial moisture content as well as from 1.05 to 20 theories of additional moisture based upon the esterification of the free acid content.

3. An improved process for the production of high molecular weight alcohols from crude esters of fatty acids having between 8 and 40 carbon atoms per molecule, comprising heating said esters with a mineral acid under essentially reflux conditions in the presence of a monohydric alcohol and dissolved in an inert organic liquid selected from the group consisting of hydrocarbons, ethers, and excess alcohol, and during the heating separating from the reaction mixture the moisture it originally contained and at least about 1.05 theories of additional water based upon esterification of the free fatty acids in the esters, and subjecting the so-treated esters to an alkali metal-reducing alcohol process to produce the corresponding alcohols.

4. An improved process for the production of high molecular weight alcohols from crude esters of fatty acids having between 8 and 40 carbon atoms per molecule, comprising heating said esters dissolved in an inert hydrocarbon liquid with sulfuric acid under essentially reflux conditions in the presence of a monohydric alcohol for about 60 minutes, and during the heating separating from the reaction mixture between about 1.05 to 20 theories of water based upon esterification of the free fatty acids and the moisture content of the starting materials, the proportion of sulfuric acid being between about 1.0 to 0.05 parts for every 100 parts by weight of fatty acid esters, and subjecting the so-treated esters to an alkali metal-reducing alcohol process to produce the corresponding alcohols.

5. An improved process for the production of high molecular weight alcohols from crude fats which comprises transesterifying said fats by reacting with an aliphatic monohydric alcohol in the presence of an alkaline alcoholysis catalyst, heating the so-transesterified fatty acid esters with a mineral acid under essentially reflux conditions in the presence of a monohydric alcohol and dissolved in an inert organic liquid selected from the group consisting of hydrocarbons, ethers, and excess alcohol for a period sufficient to generate more than the theoretical quantity of water based upon esterification of the free fatty acids, and during the heating separating the moisture content of the starting materials along with at least about 1.05 theories of said esterification water, and subjecting the so-transesterified and treated esters to an alkali metal-reducing alcohol process to produce the corresponding alcohols.

6. The process of claim 5 wherein the alkali metal-reducing alcohol process comprises reacting the so-transesterified and treated fatty acid esters with between about the stoichiometric quantity and about 5 percent in excess of that quantity of sodium and between about the stoichiometric quantity and 5 percent in excess of that quantity of methylisobutylcarbinol in the presence of between about 0.25 to 1.3 parts by weight of an inert organic liquid selected from the group consisting of hydrocarbons, ethers, and excess alcohol.

7. An improved process for the production of high molecular weight alcohols derived from tallow, which comprises heating about 100 parts by weight of said tallow dissolved in about 100 parts by weight of toluene with between about 0.2 and 0.75 parts by weight of concentrated sulfuric acid under essentially reflux conditions for a period of time between about 40 and 120 minutes, during the heating separating from the reaction mixture at least about 1.05 theories of water based upon esterification of the free fatty acids and the moisture content of the starting materials, and then reducing the so-treated esters by the sodium-reducing alcohol method.

8. The process of claim 1 wherein said inert organic liquid is a hydrocarbon.

9. The process of claim 1 wherein the quantity of water recovered is between about 2 and 10 theories.

10. The process of claim 3 wherein said inert organic liquid is a hydrocarbon.

11. The process of claim 5 wherein said inert organic liquid is a hydrocarbon.

12. A process which comprises heating about 100 parts of tallow dissolved in about 100 parts of toluene with between about 0.2 and 0.75 parts of concentrated sulfuric acid under essentially reflux conditions for a period of time between about 40 and 120 minutes and in the presence

of sufficient methylisobutylcarbinol to esterify free fatty acids and provide about 5 percent excess over the theoretical quantity required for reduction of said tallow by an alkali metal-reducing alcohol process, and during the heating separating from the reaction mixture at least about 1.05 theories of water based upon esterification of the free fatty acids of said tallow and the moisture content of the starting materials.

13. The process of claim 12 wherein the quantity of water removed is between about 2 and 10 theories.

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