Patented Feb. 7, 1950

2,496,328

UNITED STATES PATENT OFFICE

2,496,328

PROCESS OF PRODUCING POLYHYDRIC ALCOHOL ESTERS OF FATTY ACIDS

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No Drawing. Application May 2, 1947, Serial No. 745,652

7 Claims. (Cl. 260—410.7)

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The present invention relates to a process for producing monoglycerides and other hydroxy esters of fatty acids with polyhydroxy alcohols in which there is a high ratio of monoester to total ester in the reaction product.

The fatty products available commercially as monoglycerides vary somewhat in the ratio of monoglycerides to total ester content but in general the monoester content is less than 50% by weight of the total esters. The desirability of a product having a monoester content in excess of 50% and particularly in excess of 60% has been recognized by the art and attempts have been made to increase the percentage of monoesters in the reaction product.

One expedient for increasing the ratio of monoglycerides in the final product which has been suggested is to carry the reaction out in the presence of a mutual solvent for glycerine and the fatty esters, such as phenol, cresol, etc., in order to obtain a homogeneous mixture containing a high mol ratio of glycerine to fatty acids. The use of a solvent, however, has numerous disadvantages. Some of the more important of these are the difficulty of removing all of the solvent, the problem of recovering the solvent for re-use, and the loss of product in stripping operations.

It has now been discovered that a reaction product having a high monoglyceride content can be produced by completing the reaction between glycerine and fatty material with a high mol ratio of glycerine in solution or intimate contact with the fatty material and then cooling the reaction product below reaction temperatures without substantial separation of the phases.

In the process of the present invention glycerine, or other polyhydroxy alcohol which throughout the range of reaction temperatures is not soluble in the reaction product in the amounts necessary to give the desired high ratio of monoesters to total esters, is heated at an elevated temperature in contact with fats or fatty acids in the ratio of 4 to about 10 mols of said alcohol per mol of fatty acids until substantial equilibrium is reached. During this heating, or at least for a considerable period of time toward the end thereof, the contents of the reaction vessel are vigorously agitated if the polyhydric alcohol is not fully dissolved so as to give a fine emulsion thereof in the fatty material. This is practically as effective as the use of a mutual solvent in driving the reaction toward the production of the monoesters. The reaction product is then cooled under such conditions that the monoglyceride content is not substantially decreased during the cooling operation, as more fully described hereinafter.

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Any suitable apparatus may be utilized for carrying out the reaction and it is contemplated that it may be carried out continuously or batchwise. A satisfactory apparatus comprises a reaction pot or vessel provided with a jacketed wall or heating coil for heating the materials to the desired reaction temperature, a mechanical agitator which is capable of emulsifying the glycerine or other polyhydroxy alcohol in the fatty material, and an outlet leading to a cooling coil which is provided with means for maintaining the temperature thereof somewhat above the melting point of the ester product.

The starting material to provide the fatty acid content of the monoester product may be either fats or fatty acids. Among suitable fats are those of animal and vegetable origin such as tallow, fish oils, coconut oil, palm oil, palm kernel oil, Babassu oil, soy bean oil, linseed oil, olive oil, and the like and they may be pretreated by hydrogenation, refining, bleaching, etc. before they are subjected to the present process, if desired. If fatty acids are used they may be prepared from the various fats and oils by Twichellizing, by high pressure batch hydrolysis, by continuous countercurrent hydrolysis, by splitting from soap, etc. The acids may be used in substantially pure form including lauric, myristic, palmitic, stearic, oleic, linoleic, ricinoleic, etc. or they may be used in natural or artificial mixtures.

The glycerine used in the process is preferably a good grade of substantially anhydrous glycerine but this is no particularly important because the water content can be evaporated early in the reaction.

Where fats are used instead of fatty acids it is preferable to use a small amount of an alkaline catalyst to increase the rate of the reaction. While any desired alkaline catalysts may be employed, in general it is preferred to use an alkali metal hydroxide such as sodium hydroxide.

The mol ratio of glycerine to fatty acids may vary over a broad range, e. g., from about 2 to 14, but in order to obtain a product of high ratio of monoester to total ester content it is desirable to employ at least 4 mols of glycerine per mol of fatty acids and there is little practical advantage in having a ratio higher than 10 to 1. Very satisfactory results are obtained when the mol ratio of glycerine to fatty acids is approximately 5 to 1. Where this ratio is referred to in the description and claims it is to be understood as

meaning the mol ratio of the total glycerine content whether combined or free to the total fatty acids content whether combined or free.

The reaction will proceed at temperatures of the order of about 200° C. but at a relatively low reaction rate. Preferably the reaction temperature lies within the range of about 240 to 260° C. Below 240° C. the reaction time is considerably longer and the discoloration of the reaction product appears to be at least as great as that within the preferred range specified above. If the reaction temperature, on the other hand, exceeds about 260° C. there is some polymerization of glycerine, particularly in the presence of alkali metal catalyst, there is some formation of acrolein and the product is darkened unduly.

The heating at the reaction temperature is preferably continued until substantial equilibrium is reached. Within the preferred temperature range the reaction reaches equilibrium within about 1 to 3 hours whereas at about 200° C. equilibrium is reached after only prolonged heating of the order of about 4 to 12 hours.

The reaction is preferably carried out at about atmospheric pressure. It is advantageous to use a closed vessel so as to prevent contact of air with the materials at elevated temperature. It is recommended that an atmosphere of an inert gas such as hydrogen, carbon dioxide, nitrogen, etc. be provided in the reaction vessel at a somewhat positive pressure, e. g. about 2 pounds per square inch, so as to prevent any leakage of air into the system.

The solubility of the polyhydric alcohol in the fatty reaction product depends upon the composition and the temperature. Generally speaking the solubility increases with rise in temperature and decreases with increase in the chain length of the fatty acids. At about 80° C., for example, glycerine is soluble in the reaction product of glycerine with double pressed stearic acid to the extent of about 10% by weight while at about 250° C. its solubility is 2 to 3 times as great. The solubility of glycerine in glyceryl esters of the fatty acids of coconut oil, which is about 33% at 80° C., is in excess of 10 mols of glycerine per mol of fatty acids within the preferred range of 240° to 260° C. In the case of the stearate ester it is necessary to agitate the reaction mixture in order to keep 4 to 10 mols of glycerine in intimate contact with the fatty material at the temperature of operation while in the case of coconut oil esters agitation of the reaction mixture would not be necessary within the preferred operating range to maintain a high mol ration, although it is desirable to assure even heating. In the latter case, however, as the reaction mixture cools, precipitation of glycerine begins (assuming 5 mols of glycerine per mol of fatty acids were used) at about 220° C. and rapidly increasing amounts are precipitated with drop in temperature until at about 150° C. the ester layer would comprise about 67% esters and 33% glycerine by weight (a mol ratio only slightly more than 1). During normal cooling without agitation, in either of these cases, the mol ratio of glycerine to fatty acids would be far less than the desired minimum of 4 and substantial reversion of monoesters to higher esters would occur.

The prevention of back reaction after equilibrium is reached and during the cooling operation from the operating temperature to a temperature below reaction temperatures is dependent upon two factors, (1) the rapidity of the cooling step and (2) the maintenance of the high

mol ratio of glycerine in contact with the ester product. If the cooling is sufficiently rapid that the time available for back reaction is insufficient to convert a substantial portion of the monoester into higher ester it is of no particular importance to maintain the excess glycerine dissolved in or finely emulsified with the fatty product until it has been cooled below reaction temperatures. In large scale batchwise production, however, it is extremely difficult, if not impracticable, to cool a large batch of reaction product in so short a time. If the batch is discharged from the reaction vessel through a cooling coil it may take 30 minutes to an hour or more to empty it. Since an emulsion of excess glycerine in the ester product breaks rather rapidly if agitation is discontinued, very substantial back reaction could take place within the reaction vessel in that time unless agitation is continued.

It is preferred to carry out the cooling operation by contacting the reaction mixture with a surface heated a few degrees above the melting point of the ester product. A cooling coil immersed in a water bath maintained within a temperature range of about 55 to 65° C. is satisfactory and it is desirable to agitate the water bath, e. g., by introducing air at the bottom thereof, to assure uniform temperature. A shell and tube type of heat exchanger using water within the stated temperature as the cooling fluid is also satisfactory. Ordinarily if the reaction product is cooled from the operating temperature to a temperature of about 100° C. within about 15 minutes after leaving the reaction vessel, any separation which occurs within the cooling coil is of no practical significance in lowering the monoester content.

The cooled product may be run into settling tanks where the two phases separate by reason of their difference in gravity. The glycerine layer can be re-used in the process without further treatment. The ester layer may be further treated to deodorize, decolorize, and/or remove dissolved glycerine in accordance with customary practice, if desired.

For practical purposes the product may be considered to have been cooled below reaction temperatures by the time it reaches about 150° C. At that temperature, however, contact of the fatty material with air causes undesirable darkening. It is preferred to cool the product to about 100° C. or lower before exposing it to the air.

The following examples will illustrate the process of the present invention.

Example I

1800 pounds of refined coconut oil, 3870 pounds of 98% C. P. glycerine and 4½ pounds of 38% Na_2O caustic soda are mixed in a feed tank at about 93° C. and then introduced into a jacketed Dowtherm heated reaction vessel containing carbon dioxide at a pressure of 2 pounds per square inch gauge. The mixture is heated for 3 hours at a temperature of about 250° C. The reaction vessel is connected with a cooling coil having a surface area of about 175 square feet. This coil is immersed in water which is agitated by a stream of air introduced into the bottom of the water tank and the water is held at about 63° C. The reaction vessel is emptied in about 90 minutes. During the heating and emptying the contents of the vessel are thoroughly agitated by an efficient mechanical mixer. The cooled mixture at a temperature of about 93° C. is run into a settling tank. After settling, 2571 pounds of glyc-

erine are drawn off and returned to the feed tank for use in the next batch. The ester layer comprising 3045 pounds is bleached, filtered and filled into drums where it solidifies as a white fatty solid. The yield of product amounts to 2679 pounds, of which 25% by weight is glycerine. The composition of the water insoluble fraction is found to be approximately:

	Per cent
Glycerine monoesters	77
Glycerine diesters	21
Glycerine triesters, Bal. (by difference).	
Free fatty acids	1.5

The advantage of cooling the reaction product by the method of the invention is illustrated by comparing the monoester content of this batch with a similar batch which is allowed to cool in the reaction vessel and which contains only about 60% monoglycerides.

Example II

2000 pounds of double pressed stearic acid and 3530 pounds of 98% C. P. glycerine are mixed in a feed tank at a temperature of about 93° C. before being introduced into a reaction vessel where they are heated with agitation for two hours at 250° C. under a blanket of carbon dioxide at a pressure of 2 pounds per square inch gauge. After cooling and settling as described in Example I a glycerine layer of 2072 pounds is drawn off and the ester layer comprising 2647 pounds is bleached, filtered and formed into beads by spraying in a cooled tower. The bead product comprising 2455 pounds contains about 10% glycerine. The composition of the water insoluble fraction is found to be about:

	Per cent
Glyceryl monoesters	61.5
Glyceryl diesters	33.1
Glyceryl triesters, Bal. (by difference).	
Free fatty acids	1.1

A similar batch cooled in the reaction chamber contains about 57% monoglycerides. While the extent of the reversion in this instance is less than in Example I, probably because no catalyst is present, it is still substantial and important in many applications where a deviation of a few per cent may seriously affect the properties. The controlled cooling of the present invention assures uniformity in the composition of the final product which is not achieved under prior practices.

While the invention has been described in connection with certain illustrative specific examples, modifications and variations in starting materials, operating conditions and procedure are contemplated within the scope of the following claims.

We claim:

1. The process of producing polyhydric alcohol esters of fatty acids having a high monoester content which comprises heating to a temperature of at least 200° C. at least one fatty material from the group consisting of fatty acids and fatty acid esters with 4 to 10 molar proportions of polyhydric alcohol which is not miscible in these amounts with the reaction product, agitating said materials while so heated to form an intimate dispersion of said alcohol and fatty materials, subjecting the product after the reaction has reached substantial equilibrium to cooling against a surface having a temperature somewhat above the melting point of the product to reduce the temperature of the product below about 100° C. while

still substantially maintaining such dispersion, and permitting the cooled product while still liquid to separate into an ester layer containing a minor amount of dissolved polyhydric alcohol and a substantially pure layer of polyhydric alcohol.

2. The process of producing glyceryl esters of fatty acids having a high monoglyceride content which comprises heating in a reaction vessel fatty material from the group consisting of fatty acids and fatty acid esters in the presence of an excess of glycerine in the ratio of about 4 to 10 mols of glycerine per mol of fatty acids at a temperature of about 240 to 260° C. until substantial equilibrium is reached, agitating the materials during heating to maintain intimate contact between the glycerine and fatty material, withdrawing a stream of the reaction mixture from said vessel while said agitation continues, and cooling said stream of the reaction mixture sufficiently rapidly that there is no substantial reduction in monoglyceride content.

3. The process which comprises heating fat in a reaction vessel in the presence of an alkaline catalyst and an excess of glycerine at a temperature within the range of 300 to 260° C. until substantial equilibrium is reached, agitating the mixture during heating to maintain intimate contact between the fat and glycerine, withdrawing a stream of the reaction mixture from said vessel while said agitation continues, and cooling said stream of the reaction mixture sufficiently rapidly that there is no substantial reduction in monoglyceride content.

4. The process as set forth in claim 3 in which the reaction temperature is within the range of 240 to 260° C.

5. The process which comprises heating in a reaction vessel stearic acid with glycerine in the ratio of about 5 mols of glycerine per mol of stearic acid at a temperature within the range of about 240 to 260° C. for about 2 to 4 hours, agitating the mixture during heating to maintain intimate contact between the glycerine and the fatty material, withdrawing a stream of the reaction mixture from said vessel while said agitation continues, and cooling said stream of the reaction mixture sufficiently rapidly below about 150° C. that there is no substantial reduction in monoglyceride.

6. The process which comprises heating in a reaction vessel coconut oil with about 2 to 4 times its weight of glycerine in the presence of a small amount of alkaline catalyst at a temperature within the range of about 240 to 260° C. for about 2 to 4 hours, withdrawing the reaction mixture in a stream in which the ratio of glycerine to fatty material is maintained substantially constant during withdrawal and cooling said stream below about 150° C. before permitting substantial settling of the excess glycerine from the fatty product.

7. The process which comprises heating in a reaction zone fatty material in intimate contact with glycerine in the ratio of about 4 to 10 mols of glycerine per mol of fatty acids at a temperature of 200 to 260° C. until substantial equilibrium is reached, withdrawing the reaction product from said reaction zone through a heat exchanger in indirect contact with a cooling fluid at a temperature somewhat above the melting point of the product to reduce the temperature thereof below about 100° C., and maintaining an intimate admixture of unreacted glycerine with the fatty

material by agitation until at least shortly before the reaction mixture is cooled to 150° C.

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Certificate of Correction

Patent No. 2,496,328 February 7, 1950

ADAM CARR BELL ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 36, for the word "no" read *not*; column 6, line 26, for "300 to 260° C." read *200 to 260° C.*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of May, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.