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RECONSTRUCTION OF GLYCERIDE OILS

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1

The present invention is directed to the reconstruction of oils which are the glycerides of a mixture of fatty acids of varying carbon content, usually from 6 to 18 carbon atoms.

More particularly the invention is directed to the reconstruction of such glyceride oils by treatment with higher fatty acids whereby the lower fatty acids contained therein are displaced by the higher fatty acids and thus the characteristics of the initial oil are changed. In the patent to George Barsky, No. 2,182,332, dated December 5, 1939, the basic process for reconstructing such oils is described and claimed. Such a procedure is capable of giving the desired characteristics in the reconstructed oils and the present invention is intended to improve on the method there described. In the patented method, the higher fatty acid did not completely combine with the oil to displace lower fatty acids and after the operation was completed, it was necessary to remove the free fatty acids by a distillation operation. Due to the slowing of the rate of reaction towards the end thereof, a considerably longer time was ordinarily consumed in conducting the operation and because of such additional time of treatment at necessarily high temperatures, some decomposition was likely to take place, forming colored by-products which rendered the final product colored.

The present invention is intended and adapted to overcome the difficulties in the prior art, it being among the objects thereof to modify the procedure described in the aforesaid patent and to avoid the necessity of distilling out of the mixture the unreacted fatty acids.

It is also among the objects of the present invention to provide a procedure which can be adequately controlled so as to predetermine the characteristics of the final product.

In practicing the present invention, there is provided a glyceride oil of the coconut type, wherein there is a substantial amount of the lower fatty acids having 6, 8 and 10 carbon atoms. Such oils are usually either fully liquid or semi-liquid and are unsuitable in said state for conversion into a solid fat known as "hard butter." Such hard butters are largely used in industrial operations to produce edible products such as in the making of candy or other confectionery products and in baking operations. For such uses the hard butters are normally required to have specific characteristics which adapt them for the particular purpose to which they are to be applied.

In accordance with the present invention, such

2

an oil, of which babassu, palm kernel and coconut oils are the best known examples, is mixed with a higher fatty acid or usually a mixture of higher fatty acids having usually from 12 to 18 carbon atoms. The mixture is heated to a reaction temperature, usually above 250° C., whereby the lower fatty acids are removed from combination and vaporized while the added higher fatty acids enter into combination in place thereof. The free lower fatty acids are removed from the zone of reaction, leaving the reconstructed oil behind. In conducting the present operations, an excess of higher fatty acids is used over that necessary to displace the lower fatty acid. Therefore, at the end of the reconstruction, there is an excess of fatty acid present in the free state. There is then added to the reaction product a suitable amount of glycerine to combine with the free fatty acids present and the mixture is heated to cause esterification to take place, forming a neutral, or if desired, a slightly acid product.

In some cases it may be advantageous to conduct the esterification operation in two stages wherein in the first stage only part of the glycerine necessary for complete esterification of the fatty acids is added and caused to react and after said reaction is complete, the remainder of the glycerine is added and reaction finally completed. The time of the reaction is usually maintained at about 260° C. but a range of 250° to 270° C. has been found suitable to give satisfactory results. Generally the metal oxide, such as boric acid or zinc oxide is used as a catalyst so as to further the reaction without the necessity of utilizing higher temperatures. Preferably the displacement reaction is conducted in a vacuum to more effectively remove the lower fatty acids as they are evolved and thus speed up the reaction. In the esterification stage there is preferably an esterification first under atmospheric pressure with CO_2 and then under gradually reduced pressures.

The following are specific examples of the operation of the invention.

Example 1

A mixture is made of the following constituents:

	Parts by weight
Babassu oil	950
Mixed fatty acids	510

The fatty acids in this case consist of about 72% of lauric and myristic acids, 24.5% of palmitic, oleic and stearic acids, and the remainder, capric and caprylic acids.

The mixture is heated to a temperature ranging from 252° to 263° C. and a fractionating column is applied to the reaction vessel. A vacuum of about 140 mm. of mercury is applied at the beginnnig of the operation and the vacuum is gradually increased until at the end of the reaction it is about 80 mm. The heating is continued for about 3½ to 4 hours. During the reconstruction vapors of lower fatty acids displaced from the babassu oil as well as lower fatty acids contained in the fatty acid mixture are vaporized and passed through a fractionating column. The higher fatty acids are condensed therein and returned to the reaction zone.

The product has a free fatty acid value of 29%. To this product is added 40 parts of 95%–98% glycerine and the mixture heated under atmospheric pressure in the presence of a current of carbon dioxide to temperatures ranging from 245° to 265° C. After about 1½ hours a vacuum of 125 mm. is applied and this is gradually reduced during the remainder of the operation of about one hour.

The product has a free fatty acid value of 9% and there is added thereto an additional 13 parts of anhydrous glycerine. The mixture is heated as before with a vacuum starting at 175 mm. and gradually increasing to 30 mm. at the end of the operation which requires about two hours. The final product has an F. F. A. of 4.5% and is refined with caustic alkali as usual. It may be hydrogenated to give a butter having a softening point of about 28° C. The product is a fairly soft butter.

Example 2

The following constituents were placed in a reaction vessel:

	Parts by weight
Coconut oil	950
Mixed higher fatty acids	510
Zinc oxide	4

The fatty acid mixture may be the same as that used in Example 1. The reaction vessel is fitted with a fractionating column and the mixture is heated to a temperature of 253° to 263° C. A vacuum of 125 mm. is applied at the beginning of the operation and the vacuum is increased until at the end of the displacement it is 90 mm. The total time of operation is about eight hours.

The free fatty acid value of the product is 21% and to this is added 30 parts by weight of 95%–98% glycerine. A reflux condenser was applied and the vessel heated to a temperature of 243° to 262° C. A vacuum was applied, the pressure decreasing from 360 mm. to 40 mm. at the end of the operation, which requires about 3½ hours.

The free fatty acid value of the partially esterified product is about 8% and to this is added 12 parts of glycerine. Heating is continued with the application of a refluxed condenser at temperatures of 245° to 268° C. with a vacuum of 360 mm. with an increase in the vacuum to 12 mm. at the end of the operation. Towards the end of the operation the reflux condenser is removed and the total time of the second esterification is about 2¼ hours. The final product has a F. F. A. of about 4%. The reconstruction, namely, the removal of the fatty acids having 6, 8 and 10 carbon atoms from the reaction mixture which includes the lower fatty acids present both in the coconut oil and in the fatty acid mixture, is about 93%.

The product is refined as usual and hydrogenated, the butter having a softening point of about 33.5° C. The characteristics of this product are such as to render it highly adapted for use in chocolate coatings.

Example 3

The mixture of constituents is the same as in Example 1, with the addition of 7 parts by weight of zinc oxide as a catalyst. The operation is conducted with the fractionating column and a temperature is maintained in the reaction vessel of 256° to 262° C. A vacuum of 140 mm. is applied at the beginning of the operation and this is gradually increased to 105 mm. at the end of the reaction. The time of heating is about 12 hours.

The product has a free fatty acid value of 20.5%. To this is added 30 parts by weight of glycerine and a temperature of 255° to 267° C. maintained with the use of carbon dioxide at atmospheric pressure. After about 3 hours a vacuum is applied, which is gradualy increased to 25 mm. at the end of the operation which requires a total of about 6 hours. The F. F. A. of the product is 5% and is refined as usual and hydrogenated. The softening point of the hard butter is about 33° C.

Example 4

The following mixture of constituents is made:

	Parts by weight
Palm kernel oil	650
Mixed stearic-palmitic acids	290
Boric acid	12

The mixture is placed in a reaction vessel fitted with a fractionating column and heated to a temperature in the vessel of about 270° C. A vacuum of 200 mm. is maintained. The vapors passing through the fractionating column have a temperature of 180° to 185° C. After five hours of operation the vacuum is increased to 90 mm. and the reaction is stopped when the free fatty acid value of the product has dropped to 20–21%.

A sufficient amount of glycerine is added to lower the free fatty acid value to 6%. It is maintained at a temperature of 260° C. with a reflux condenser so adjusted as to return vaporized glycerine to the reaction vessel but to allow water vapor to escape. A vacuum of 200 mm. is utilized and it is gradually increased to 15–20 mm. and maintained at this point until the F. F. A. is 6%. The reflux condenser is removed and distillation with steam conducted until the F. F. A. is reduced to 4%. The final product is refined as usual and the hard butter has a softening point of 34.2° C.

There are numerous advantages inherent in the present procedure. There is eliminated the necessity for removing relatively large quantities of uncombined fatty acids after the reconstruction. This greatly simplifies the operation and reduces the cost thereof. It permits the use of greater quantities of higher fatty acids in the reconstruction operation, thereby enabling a higher degree of reconstruction to be obtained and enabling one to produce harder butters than was possible by prior methods. One may also use higher fatty acid fractions containing substantial amounts of the lower fatty acids and the operation can proceed smoothly and effectively with the elimination of as much of the lower fatty acids as is desired to give predetermined characteristics to the product. The esterification of the excess fatty acid avoids the necessity of a distillation which may cause decomposition and discoloration to take place in the product. The operation is smoother and relatively lower temperatures can

be used in the operation than heretofore, whereby danger of discoloration is further reduced. The two-stage process described herein is also advantageous as it allows a better control of the entire operation.

Although the invention has been described setting forth several specific examples of the operation, various changes in the details may be made within the principles herein set forth. For instance, the invention is applicable to oils of other types than the coconut type wherein there are acids of higher and lower carbon content and the lower acids are to be displaced by higher. In the process it is not necessary to use a mixture of higher fatty acids but single fatty acids are applicable. Both saturated and unsaturated higher fatty acids may be used and the final product need not necessarily be hydrogenated. The mixture of higher fatty acids used in the operation may contain minor quantities of the lower fatty acids or they may be entirely free therefrom.

The temperatures used, the time of operation, the character of the catalyst, the amount of vacuum, and various other details inherent in the procedure may be varied as is well-known in the art. These and other changes in the details may be made within the spirit of the invention which is to be broadly construed and not to be limited except by the character of the claims appended hereto.

I claim:

1. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

2. A method of reconstruction glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, adding a metal oxide catalyst, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

3. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, adding zinc oxide catalyst, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

4. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%, said displacement reaction being conducted in a vacuum.

5. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%, said displacement reaction being conducted in a vacuum and at least part of said esterification being conducted in a vacuum.

6. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature of 250° to 270° C. to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

7. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%, the temperature at both said stages being from 250° to 270° C.

8. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids

having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product, and thereafter introducing a further amount of glycerine and heating to cause further esterification until the acid value is about 5–6%.

9. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, said higher fatty acid containing a small amount of said lower fatty acid, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

10. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, continuing said reaction and removal until at least 90% of the acids having less than 12 carbon atoms is removed from the reacting mixture, thereafter introducing glycerine into the reaction product until the acid value is about 5–6%, and heating to cause esterification of said glycerine with said product.

11. A method of reconstructing glyceride oils which comprises mixing a coconut type oil the fatty acid radicals of which have from 6 to 18 carbon atoms with a mixture of higher fatty acids having from 12 to 18 carbon atoms in excess of that necessary to displace the lower fatty acids of said oil, heating the mixture to a reaction temperature to displace a major portion of the lower fatty acids having 6 to 10 carbon atoms and to cause said higher fatty acids to enter into combination in said glyceride oil, removing the latter from the zone of reaction, fractionating said vapors and condensing and returning higher fatty acid to said mixture, thereafter introducing glycerine into the reaction product, and heating to cause esterification of said glycerine with said product until the acid value is about 5–6%.

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