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FAT CRYSTALLIZATION PROCESS

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This invention relates to an improved crystallization process. More particularly, it relates to the addition of certain crystal modifying agents to glyceride oils containing fatty materials which are insoluble in the oils, whereby separation of the insoluble fatty materials from the oils is facilitated.

A large amount of vegetable glyceride oil is used as salad oil. Such oils can serve as a base for various liquid salad dressings, providing an oily coating for salad ingredients. They are also used in mayonnaise emulsions. Both salad oils and mayonnaise are usually kept under refrigeration by the housewife. At temperatures of about 40° F. or lower, fatty materials will deposit out of many salad oils, causing them to have a cloudy appearance. In mayonnaise, such crystal formation tends to break the emulsion, causing separation of fatty material from the aqueous portion.

If soybean oil is used as a salad oil it tends to develop a characteristic "beany" odor and flavor. Even when it has been rendered completely odorless and flavorless by high-temperature steam deodorization, the characteristic odor and flavor will return, in part, at least, due to the linolenic acid content of the oil.

It has been proposed that the stability of soybean oil against odor and flavor reversion can be increased by hydrogenation. However, hydrogenation decreases the unsaturation of unsaturated component fatty acids and also converts the unsaturated acids to higher-melting and less-soluble isomers. The oil must then be "winterized" by a process including cooling and subsequent separation of insoluble glycerides to remove materials which will solidify when the oil is refrigerated, and thereby cause undesirable salad oil performance and appearance. Other oils such as cottonseed oil are given a similar winterizing treatment. Insoluble fatty materials in oils such as corn oils are also removed by a cooling step, followed by a separation step.

Another important use of glyceride oils is in the paint industry. Oils of particular interest are the so-called "drying oils" which form protective coatings because of the ability of these oils to polymerize or "dry" after they have been applied, thereby forming tough, adherent, impervious and abrasion-resistant films.

It is generally believed that the film-forming properties of drying oils are related to their degree of unsaturation, and that the films are formed by polymerization of double bonds present in unsaturated oils. It is highly desirable, therefore, that oils suitable for use as drying oils contain a large amount of triunsaturated glycerides, and relatively few trisaturated glycerides or mixed saturated-unsaturated triglycerides.

U.S. Patents 2,442,531 and 2,442,533, issued to E. W. Eckey on June 1, 1948, disclose the directed rearrangement of triglycerides. By means of the process disclosed in these patents a substantial portion of mixed saturated-unsaturated triglycerides is rearranged to form a larger proportion of highly saturated glycerides and highly unsaturated glycerides. The more saturated glycerides in crystalline form are then separated from the rearranged mixture, leaving an unsaturated oil very suitable for use as a drying oil.

Special coating fats are required for coating of candies.

These fats must have a high melting point so that they will not be greasy at normal room temperatures. However, these fats must also melt in the mouth when the candy is eaten, and thus the presence of fats melting at too high temperatures are undesirable. When oils such as hydrogenated palm kernel oil, and palm oil, either hydrogenated or unhydrogenated, are to be used for this purpose, it may be desirable to separate out highly-saturated materials which would produce a waxy taste in the mouth. Suitable confectioner's fats can also be formed from the more saturated portions of directed rearranged triglycerides.

At times it would be desirable to use palm oil as a major constituent of a margarine oil. In certain geographic locations palm oil is cheaper than other oils, and a supply of palm oil may be more readily available than a supply of some other oil. It has been found that the content of high-melting insoluble fats in palm oil, at a temperature of 92° F., is too high to produce a satisfactory margarine, since these insoluble fats will impart a waxy taste in the mouth during eating. Separation of the insoluble fats from the palm oil would increase its utility as a margarine constituent.

One of the main problems encountered in the separation of insoluble fatty materials from glyceride oils has been the fact that the insoluble fatty materials entrain a large amount of glyceride oil. In addition, conventional separation procedures are very low.

It has now been found that by the process of this invention the separation of insoluble fatty materials from liquid glyceride oils is greatly facilitated, thereby permitting the recovery of a much larger amount of liquid oil than has heretofore been possible. In addition, the rate of separation is greatly increased. As used herein the term "insoluble fatty materials" is intended to include materials which dissolve in oils at elevated temperatures and which will precipitate out of solution as the oils are cooled and allowed to stand.

It is therefore an object of this invention to provide a process for modifying insoluble fatty materials in glyceride oils whereby the subsequent separation of the fatty materials is greatly facilitated.

It is a further object of this invention to provide an improved process for making a salad oil.

Another object is to provide an improved method of making a drying oil.

Yet another object is to provide a method of making confectioners' fats which have good eating quality.

Other objects and advantageous features will be apparent from the following detailed description.

In general, the process of this invention comprises the steps of dissolving in a glyceride oil containing insoluble fatty material, at a temperature at which substantially all of said fatty material is in solution in said glyceride oil, from about 0.001% to 0.5%, by weight of oil, of sucrose esterified with an average of at least one saturated fatty acid having from 12 to 22 carbon atoms in the alkyl chain, at least one short-chain fatty acid having from 1 to 6 carbon atoms in the alkyl chain, the total short-chain fatty acid content being equal to from 5% to 100% by weight of the total long-chain fatty acid content; cooling the glyceride oil to a temperature at which insoluble fatty material comes out of solution; and separating the insoluble fatty material from the oil. The degree of esterification should be such that the ester contains an average of not more than about 5 unesterified hydroxyl groups per sucrose molecule. Esters containing more than that number of unesterified hydroxyl groups will be too insoluble to modify the fatty materials in the desired manner.

The sucrose ester exerts a modifying effect on the insoluble material so that it comes out of solution in the form of large crystalline aggregates. These entrain a

smaller amount of liquid fatty glycerides during separation than do crystals formed in the absence of ester.

The process of this invention is generally applicable to any glyceride oils which contain fatty materials which will dissolve in the oils at elevated temperatures and which will crystallize out of solution when the oils are subsequently cooled and allowed to stand. For example, the removal of insoluble fatty materials from oils which are conventionally "winterized" to form salad oils, such as cottonseed oil, hydrogenated soybean oil, and corn oil is greatly facilitated. The process can be applied to oils such as palm oil and palm kernel oil, either hydrogenated or unhydrogenated to form improved margarine oils or confectioners' fats.

Directed rearranged triglycerides can also be processed by this invention. Preferably the directed rearrangement is carried out as described in U.S. Patent 2,442,531, issued June 1, 1948, in which triglyceride oils are contacted with a low-temperature molecular rearrangement catalyst at such a temperature that the more highly saturated triglycerides are precipitated as they are formed during the rearrangement of the glycerides in the oil. A list of suitable rearrangement catalysts is set forth in the aforementioned U.S. Patent 2,442,531. However, it is to be understood that other suitable rearrangement catalysts and operating conditions can be used. As used herein the term "directed rearrangement" is intended to denote a molecular rearrangement process directed for a greater yield of highly saturated and highly unsaturated glycerides than would be found in an oil having a random distribution of fatty acid triglycerides.

The sucrose esters can be formed by direct esterification of sucrose with fatty acids, fatty acid anhydrides, or fatty acid halides. They can also be prepared by interesterification of sucrose with fatty acid esters of other polyhydric compounds in the presence of suitable solvents such as pyridine, amides, and sulfoxides. Other methods of forming these esters can be used, and it is to be understood that the invention is not limited to any specific method of making the esters.

It is preferred that the oils to be processed be heated to a temperature at which substantially all of the insoluble fatty material is in liquid form prior to slowly cooling the oil in which is dissolved the sucrose ester. The ester can be added prior to or after heating. The exact conditions for cooling will vary with the amount of oil in the batch and the amount of insoluble fatty material, but the optimum cooling conditions can be determined by those skilled in conventional oil graining procedure.

The insoluble fatty materials are conveniently separated by conventional filtration procedures, but other methods of separation such as centrifuging, can be used.

The improved results which can be achieved by the process of this invention are clearly illustrated by the following examples:

EXAMPLE I

250 g. of refined and bleached soybean oil, hydrogenated to an iodine value of about 105, was mixed in a container with 0.1%, by weight of oil, of sucrose diacetyl monopalmitate. This ester was the reaction product of 1 molecule of acetic anhydride and 1 molecule of sucrose monopalmitate. The ester contained an average of two acetyl and one palmitoyl groups per molecule of sucrose.

The mixture of oil and additive was heated to 140° F. for one hour. It was then placed for 3 days in a room held at a temperature of 40° F. The resulting mixture of liquid and solid glycerides which had formed was filtered through a Büchner funnel using filter paper and suction. The following measurements were recorded of the total amount of oil passing through the filter at various time intervals, as compared with a similar sample containing no additive:

Time (min.)	Filtrate Volume (cc.)	
	No Additive	Sucrose acetyl palmitate
1	71	80
2	112	125
6	144	150
10	146	157

The iodine value of the two filtrates were substantially the same, showing that the increased filtration was due to crystal modification and not a decrease of amount of crystals.

As can be seen by the above data the addition of sucrose fatty ester increased the filtrate volume, clearly demonstrating the increase in yield which can be obtained by addition of sucrose fatty ester prior to cooling the hydrogenated soybean oil.

A comparable improvement in separation can also be obtained by substituting in the example esters containing myristic, stearic, arachidic or behenic acid, or mixtures of these acids in combination with or in place of the palmitic acid, and additionally, butyric, propionic, valeric or caproic acids and mixtures thereof in combination with or in place of the acetic acid. In general, a decrease in the number of unesterified hydroxyl groups will result in improved results.

EXAMPLE II

An ester of sucrose containing an average of about four acetic acid groups and about four palmitic acid groups per molecule of sucrose was dissolved in a one-pound sample of refined cottonseed oil at a level of 0.005% by weight. This oil, and also a sample of the oil without ester, were heated to a temperature of 140° F. with stirring. The samples were allowed to cool gradually and held at 50° F. for about three days and then were cooled to 40° F. and held at that temperature for about 24 hours to insure complete crystallization. Each sample was vacuum filtered using a Büchner funnel and filter paper. The filtration was continued until the filter cake broke. The filtrates were weighed and the yields of oil calculated. These data were as follows:

Amt. Additive (percent)	Filtration Time (min.)	Yield of Oil (gm.)	Yield of Oil (percent)
None	265.0	296	66.2
0.005	112.5	305	68.2

A comparable improvement in filtration will be noted when esters of the foregoing examples are used with other oils such as corn oil and directed rearranged glyceride oils.

The practice of the process of this invention in the removal of fatty materials which are insoluble in glyceride oils at higher temperatures is illustrated by the following example:

EXAMPLE III

Soybean oil was hydrogenated to an iodine value of 105 and winterized by holding it at 50° F. for 2 weeks and then holding it at 40° F. for three days. The oil was then vacuum filtered. A mixture was formed containing 95% of the clear oil filtrate and 5% of a saturated triglyceride containing about 2 palmitic acid groups and 1 stearic acid group per molecule. This saturated triglyceride had an iodine value of 0.012. To the mixture was added 0.1%, by weight, of the sucrose ester of Example I. 250 gm. samples of the oil mixture with and without added ester were heated to 140° F. for one hour to destroy all crystal nuclei and then cooled to 80°

F. and held at that temperature for three days to permit crystals to form. The resulting mixtures of insoluble fatty material and glyceride oil were filtered through a Büchner funnel using filter paper and vacuum. The following measurements were recorded of the total amounts of oil passing through the filter at various time intervals:

Time (min.)	Filtrate Volume (cc.)	
	No Additive	Sucrose Ester Added
½	30	50
1	48	72
2	70	105
3	87	128
5	(1)	160
10	(1)	190
15	175	200

[1] Not measured.

Comparable results will be achieved by substitution in the foregoing example of oils such as directed rearranged glyceride oils, hydrogenated vegetable oils and other glyceride oils containing fatty materials insoluble in these oils at higher temperatures.

Although it is to be understood that the invention is not to be limited by any theory, it is believed that esters suitable for improving the filtration of oils for the purpose of separating insoluble fats from oils should contain a substrate-similar and a substrate-dissimilar moiety in the molecule. In the case of the aforementioned systems fatty acid chains in the fats and in the sucrose ester are similar. The sucrose portion of the additive represents a polyhydric compound which is dissimilar from that of the fats.

It is also believed that it is important that materials added as filtration aids bear some relation in melting point and/or solubility to the fats which are to be separated by filtration. These aids should be made with fatty acids having neither too high nor too low a melting point, so that the modifier will have a tendency to deposit on the incipient crystal nuclei as they are formed, thereby modifying the fat crystals. This results in the formation of crystal aggregates (around a crystallization center) which are compact and not feathery and are more easily filtered.

Further, it is believed that if the additive has too high a melting point or too low a solubility in the oil, nuclei of additive will tend to form before the fat nuclei are formed, and the additive may act as a nucleating agent for the fat, forming more nuclei than would normally appear in the fat. As a result the fat crystal aggregates will be more numerous and filtration will be more difficult.

Although specific examples have been given to illustrate the invention, it is to be understood that the invention is not to be limited to these examples, and that variations in the processing conditions which will suggest themselves to those skilled in the art are intended to be within the scope of the invention. It will further be appreciated that sucrose esters used in the practice of this invention usually will be a mixture of various esters and that the specified proportions of fatty acids represent average values for such mixtures.

This is a continuation-in-part of application S.N. 845,641, filed October 12, 1959.

What is claimed is:

1. The method of separating insoluble fatty material from glyceride oil which comprises the steps of dissolving in said glyceride oil, at a temperature at which substantially all of said fatty material is in solution, from about 0.001% to 0.5%, by weight of oil, of sucrose esterified with an average of at least one saturated fatty acid having from 12 to 22 carbon atoms in the alkyl chain, at least one short-chain fatty acid having from 1 to 6 carbon atoms in the alkyl chain, the total short-chain fatty acid content being equal to from 5% to 100% by weight of the total long-chain fatty acid content, said ester containing not more than 5 unesterified hydroxyl groups; cooling the glyceride oil to a temperature at which insoluble fatty material comes out of solution; and separating the insoluble fatty material from the oil.

2. The method according to claim 1 wherein a solution of sucrose ester in oil is heated to a temperature at which substantially all of the insoluble fatty material is dissolved, the sucrose ester is dissolved in said heated oil, and the resulting mixture is slowly cooled to a temperature at which fatty crystals will form.

3. The method according to claim 1 wherein the oil is heated to a temperature at which substantially all of the insoluble fatty material is dissolved, the sucrose ester is dissolved in said heated oil, and the resulting mixture is slowly cooled to a temperature at which fatty crystals will form.

4. The method according to claim 1 wherein the sucrose ester is an acetyl palmitoyl sucrose.

5. The method according to claim 1 wherein the oil is cottonseed oil.

6. The method according to claim 1 wherein the oil is hydrogenated soybean oil.

7. The method according to claim 1 wherein the oil is a directed rearranged glyceride oil.

References Cited in the file of this patent

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