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SALAD OILS AND METHOD OF MAKING THEM
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This invention relates to improved salad oils. More particularly, it relates to oils which can be stored at relatively low temperatures for extended periods of time without clouding, and which are capable of being used in preparing mayonnaise emulsions which themselves can be stored at low temperatures.

Oils which are suitable for salad use are frequently stored in refrigerators. The cooling of such oils to temperatures encountered in refrigerators, such as about 40° to 50° F., results in the deposition of crystalline material, usually solid triglycerides, from the oil. This material may appear in the form of a cloud, or as a group of crystals, and is considered objectionable by the housewife. The tendency to form solid glycerides in oils also adversely affects the suitability of the oil for use in mayonnaise emulsions. Mayonnaise emulsions prepared from such oils tend to be unstable at low temperatures and are more easily broken.

Frequently it is desirable to hydrogenate natural vegetable oils, such as soybean oil, in order to improve their oxidative stability. This hydrogenation will tend to raise the melting point and to produce components of decreased solubility in the oils, causing them to have the undesirable properties listed hereinbefore.

A large proportion of the undesirable material can be removed from oils by the process known as "winterizing" in which the oils are carefully cooled to low temperatures for extended periods of time to permit precipitation of solid material. Such solids can then be removed by pressing or other separation procedures. However, not all of the high-melting solid material is removed from the oils by this processing, and the oils still tend to cloud when stored for extended periods of time at low temperatures.

It has now been found that under the present invention the time for storage at low temperatures without clouding can be greatly extended for salad oils.

Accordingly, it is an object of this invention to provide an improved salad oil which will remain free from clouding or crystal formation for longer periods of time than will oils which have been merely treated by conventional winterizing techniques.

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

The testing procedure for oils as used hereinafter involves holding the oil at a temperature of about 30° F. until a cloud forms in the oil. As used herein, the term "chill test" is intended to define the length of time, after cooling the oil to 30° F. (unless some other temperature is specified), until such a cloud forms.

In general, oils of this invention comprise a clear base salad oil containing dissolved therein at least 0.001% by weight, of disaccharide fatty ester. The disaccharide should be esterified with an average of from about 15% to 85%, based on the total fatty acid in the ester, of saturated fatty acid having from 14 to 22 carbon atoms. The remainder of the fatty acid is selected from the group consisting of fatty acids having from 2 to 12 carbon atoms, or unsaturated fatty acids having from 14 to 22 carbon atoms. The ester must have an average of not more than 5 unesterified hydroxyl groups per molecule.

It will be appreciated that disaccharide ester used in the practice of this invention usually will be a reaction

product containing a mixture of different esters. For this reason, the invention is defined in terms of average fatty acid content per molecule.

By way of example, a suitable ester for this invention is sucrose esterified with an average of 6 palmitic acid groups and 2 oleic acid groups. Other long-chain saturated fatty acid groups such as those of myristic, stearic, arachidic, or behenic acids, and mixtures thereof, can be present in the ester in place of part or all of the palmitic acid groups. Since the sucrose ester must have an average of not more than about 5 free hydroxyl groups, the sucrose can be esterified additionally with short-chain fatty acids such as acetic, propionic, butyric, caproic, caprylic, capric, lauric, and/or lauroleic acids, or with long-chain unsaturated fatty acids such as myristoleic, palmitoleic, oleic, linoleic, linolenic, gadoleic, arachidonic, erucic, elaidic, clupanodonic, and/or brassidic acids. Maltose and lactose are examples of other disaccharides which can be used to form esters suitable for use in the practice of this invention.

A wide variety of oils can be used as base salad oils in the practice of this invention, either individually or as mixtures of oils. Included among suitable oils are the so-called natural salad oils such as olive oil, sunflower seed oil, safflower oil, and sesame oil. Oils such as cottonseed oil and corn oil must be given a preliminary "winterizing," dewaxing, or similar other treatment to remove the higher-melting solids to form a good base salad oil. Other oils, such as soybean oil, may require some hydrogenation to prevent rancidity with prolonged storage, and the higher-melting glycerides formed during this hydrogenation treatment should be removed. Base salad oils can also be formed by directed, low-temperature inter-esterification of animal and vegetable fatty materials, followed by removal of higher-melting glycerides formed during the reaction (U.S. Patent 2,442,532, issued June 1, 1948, to E. W. Eckey). Another group of oils includes those in which one or more short-chain fatty acids replace the longer-chain fatty acids present in natural triglyceride oils. Other base salad oils will suggest themselves to those skilled in the art, provided they have a suitable chill test as hereinbefore defined. As used herein the term "base salad oil" is intended to include any salad oil which will not form solids immediately when cooled to 30° F.

The disaccharide esters suitable for use in this invention can be prepared by a variety of methods. For example, a disaccharide can be reacted with mixtures of acid chlorides of suitable fatty acids. Sucrose can also be catalytically esterified with mixtures of methyl esters of suitable fatty acids. It is to be understood, however, that the invention is not to be limited to any specific method of preparation of the disaccharide ester.

The ester and the base salad oil can be mixed together in any convenient manner. For example, ester in liquid form can be mixed with the oil. If the ester is in solid form, it can be dissolved in the oil, although it may be desirable to heat the oil or the mixture of oil and ester to facilitate solution. It is to be kept in mind, however, that in all cases the resulting product is merely a physical mixture and there is no chemical reaction between the ester and the oil.

The following examples will serve to further illustrate the invention.

Example 1

Sucrose was substantially completely esterified by reaction with palmitoyl and oleoyl chlorides in the presence of a dimethyl formamide-pyridine mixture. Upon analysis the reaction product was found to have an average composition per molecule of sucrose, of about 0.3 unesterified hydroxyl group, 6 molecules of palmitic acid, and 1.7 molecules of oleic acid. The ester was

3

added to samples of a mixture containing 90% winterized cottonseed oil and 10% unwinterized cottonseed oil. This oil had a chill test of 14 hours at 30° F. When indicated percentages of the ester were added to the oil samples, the following chill test results were noted:

Amount of ester (percent by weight)	Chill test (hours at 30° F.)
None -----	14
0.01 -----	55
0.1 -----	200
0.2 -----	200
0.3 -----	400

A slight milkiness was noted in the oil at the three highest concentrations. This was due to the presence in the ester of small proportions of compounds of very high palmitic content which apparently do not exert any seeding effect, and do not interfere with the inhibiting action of the ester. A similar improvement in chill test will be noted on using similar esters where various saturated and unsaturated long-chain fatty acids as hereinbefore specifically described replace the palmitic and oleic acids.

Example II

Refined and bleached cottonseed oil was winterized by storing it at 40° F. for 5 days and then removing the crystals which had formed by vacuum filtration. The sucrose ester of Example I was added to this oil at levels of 0.02% and 0.005% by weight. The mixture was heated to 275° F. with continuous stirring. The heated materials were placed in 4-oz. bottles, which were then corked and sealed with paraffin. The bottles were placed in an ice bath, together with bottles containing the oil without additive, and inspected at regular intervals. The following chill test results were noted.

Amount of ester (percent by weight):	Chill test (days at 32° F.)
None -----	2
0.005 -----	>5
0.02 -----	>10

Example III

The same ester which was used in Example I was added, at a level of 0.005%, by weight, to refined and bleached soybean oil which had been hydrogenated to an iodine value of 107 and then winterized. The oil containing the additive had a chill test at 32° F. of greater than 7 days, while the oil without additive had a chill test of only 4 days.

Example IV

A sucrose ester was made containing an average of about 3.7 palmitic and 3.6 acetic acid groups, and 0.7 unesterified hydroxyl groups per molecule of sucrose. 0.1% of this ester was added to an oil similar in composition to that used in Example I. The chill test of the oil alone at 30° F. was 12 hours, but the oil containing the additive had a chill test of about 100 hours. A similar improvement will be noted when various long- and short-chain fatty acids as hereinbefore specifically described, replace the acetic and palmitic acids in the ester.

Example V

A sucrose ester was made containing an average of 3.7 palmitic and 4.0 oleic acid groups and 0.3 unesterified hydroxyl groups per molecule of sucrose. This ester was tested at a level of 0.1%, in an oil having properties similar to that of Example IV, and resulted in a chill test of about 80 hours for the oil.

Example VI

A salad oil was formed by randomly interesterifying a mixture of 246 lbs. each of cottonseed oil and triacetin. Excess triacetin was removed by deodorizing the interesterified product. This oil had a chill test of less than 1½ hours at 30° F. An ester was formed by interester-

4

ifying sucrose with a mixture of hydrogenated soybean and cottonseed oils. The fatty acid content in the ester comprised about 8.4% palmitic, 8.4% stearic, 75.0% monoenoic, 7.9% dienoic, and 0.3% trienoic acids. The ester contained an average of about 5 free hydroxyl groups per molecule of sucrose. A sample of the salad oil containing 0.1% of the sucrose ester was found to have a chill test at 30° of 14 hours. Similar results can be obtained by adding the ester to salad oils formed by the random interesterification of tripropionin, tributyrin, tricaproin, or tricaprylin with cottonseed or other vegetable oils.

Example VII

An ester was formed by reaction of a mixture of palmitoyl and elaidoyl chlorides with sucrose. The ester was substantially completely esterified and contained an average of about 3.6 palmitic and 3.7 elaidic acid radicals and 0.7 unesterified hydroxyl groups per molecule of sucrose. 0.1% of this ester was dissolved in a winterized cottonseed oil having a chill test of about 10 hours. The resulting product had a chill test of about 45 hours.

Example VIII

An ester was formed by the reaction of sucrose with palmitoyl and acetyl chlorides, and contained an average of about 2.9 palmitic and 2.5 acetic acid radicals and 2.6 unesterified hydroxyl groups per molecule of sucrose. When 0.1% of this ester was dissolved in the winterized oil used in Example VII the chill test was increased to 104 hours.

Example IX

An ester was formed by the reaction of palmitoyl and acetyl chlorides with sucrose, and contained an average of about 1.6 palmitic and 1.9 acetic acid radicals and 4.5 unesterified hydroxyl groups per molecule of sucrose. When 0.1% of this ester was dissolved in the winterized cottonseed oil used in Example VII the chill test was found to be 24 hours.

Example X

A mixture of cottonseed and soybean oils was hydrogenated to an iodine value of 70 and then converted to methyl esters by interesterification with methanol. The methyl esters were then interesterified with sucrose. The fatty acids in the ester comprised about 8.4% palmitic, 8.4% stearic, 75.0% monoenoic, 7.9% dienoic, and 0.3% trienoic acids, and the ester contained an average of about 3.4 unesterified hydroxyl groups per molecule of sucrose. A solution of 0.1% of this ester in the winterized cottonseed oil of Example VII formed a product having a chill test of 40 hours.

Example XI

An ester was formed by reacting lactose with equimolar portions of palmitoyl and acetyl chlorides. The ester contained an average of 0.5 unesterified hydroxyl groups, 4.1 palmitic and 3.4 acetic acid radicals per molecule of lactose. When 0.1% of this ester was dissolved in a winterized cottonseed oil having a chill test of about 10 hours, the chill test of the oil was increased to 101 hours.

Example XII

An ester was prepared by reacting equimolar portions of palmitic and acetic acid chlorides with maltose in a pyridine solvent. The ester contained an approximate average composition of about 1.5 unesterified hydroxyl groups per molecule of maltose and ester contained approximately equal amounts of palmitic and acetic acid radicals. 0.1% of this ester was dissolved in a winterized cottonseed oil having a chill test of about 10 hours, and the resulting product was found to have a chill test of 29 hours.

Example XIII

Soybean oil was hydrogenated to an iodine value of

about 104 and winterized to form an oil having a chill test of 12 hours at 30° F. To this oil was added 0.1%, by weight, of sucrose ester containing about 4 palmitic and 4 acetic acid radicals per molecule. The oil containing the ester had a chill test of 125 hours at 30° F.

Although it is desired not to be bound by any theory, it is believed that inhibition of the formation of crystalline material in oil is accomplished by selecting a material which, at the temperature at which protection is desired, will be substantially dissolved in the oil, but the amount of inhibitor added preferably should be at a level not far below that at which precipitation of the inhibiting material in the oil will occur. It is believed that the inhibitor acts by being adsorbed on the invisible crystal nuclei of the higher-melting components of the substrate oil, so that further crystallization of these components is greatly retarded. Materials having strong tendencies to be adsorbed can be added at lower levels than materials with weaker adsorptive tendencies.

A proper balance is required for the optimum inhibition of a system—a balance between solution tendency as particularly promoted by unsaturated (or low molecular weight) chain on the ester and adsorptive tendency as promoted by saturated chains. It would be presumed that since trans-unsaturated chains are intermediate between cis-unsaturated and saturated chains in their usual effect on solubility or melting level, they would also be intermediate in their effect on inhibition action. Experimental work has indicated, however, that cis- and trans-chains appear to be comparable in their effect on inhibition power.

If too large an amount of inhibitor is present, it will precipitate out of solution and possibly even promote crystallization of high-melting solids in the oil. Too small an amount of inhibitor, of course, will be relatively ineffective. Thus, a disaccharide completely esterified with long-chain saturated fatty acids will be too insoluble to inhibit effectively crystallization of high-melting glycerides in oil at 30° F. However, a disaccharide esterified partly with long-chain saturated fatty acids and partly with unsaturated long-chain fatty acids or with short-chain fatty acids can generally be used in sufficient concentrations without precipitating out, and will provide very satisfactory crystal inhibition. Amounts of ester in excess of about 0.5%, by weight, are unnecessary as affording no significant added improvement of the oil.

This is a continuation-in-part of application Serial No. 104,004, filed April 19, 1961, now abandoned.

What is claimed is:

1. A clear glyceride salad oil having superior resistance to deposition of high-melting solids and comprising a base salad oil having dissolved therein at least about 0.001%, by weight, of disaccharide fatty acid ester, the disaccharide being esterified with an average of from about 15% to 85%, based on the total fatty acid in the ester, of saturated fatty acid having from 14 to 22 carbon atoms, the balance of the fatty acid being selected from the group consisting of fatty acids having from 2 to 12 carbon atoms and unsaturated fatty acids having from 14 to 22 carbon atoms, said ester having an average of not more than 5 unesterified hydroxyl groups per molecule.
2. A salad oil according to claim 1 wherein the disaccharide is sucrose.
3. A salad oil according to claim 1 wherein the fatty acid groups comprise acetic and palmitic acid groups.
4. A salad oil according to claim 1 wherein the fatty acid groups comprise palmitic and oleic acid groups.
5. A salad oil according to claim 1 wherein the fatty acid groups comprise palmitic, stearic, monoenoic, dienoic, and trienoic acid groups.
6. The method of retarding the deposition of high-melting solids from salad oils which comprises dissolving in a clear base salad oil at least 0.001%, by weight, of disaccharide fatty acid ester, the disaccharide being esterified with an average of from about 15% to 85%, based on the total fatty acid in the ester, of saturated fatty acid groups having from 14 to 22 carbon atoms, the balance of the esterifying material being selected from the group consisting of fatty acids having from 2 to 12 carbon atoms and unsaturated fatty acids having from 14 to 22 carbon atoms, said ester having an average of not more than 5 unesterified hydroxyl groups per molecule.
7. The method according to claim 6 wherein the disaccharide is sucrose.
8. The method according to claim 6 wherein the fatty acid groups comprise acetic and palmitic acid groups.
9. The method according to claim 6 wherein the fatty acid groups comprise palmitic and oleic acid groups.
10. The method according to claim 6 wherein the fatty acid groups comprise palmitic, stearic, monoenoic, dienoic, and trienoic acid groups.

References Cited in the file of this patent

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