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STABILIZED SALAD OILS

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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 prolonged cooling of such oils to temperatures normally encountered in refrigerators, such as from about 40° to about 50° F., generally 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 high melting glycerides 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 temperature. Moreover, the usual winterizing treatment undesirably tends to remove by entrainment a substantial portion of the olein fraction of the oil.

It has now been found that by means of 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 either have been merely treated by conventional winterizing techniques or have not been winterized.

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 a crystal inhibiting amount and at least 0.001% by weight, of fatty ester of monosaccharidic material having an oxide ring structure and selected from the group consisting of aldohexose, aldohexuronolactone, aldohexonolactone, methyl aldohexoside, and aldohexuronic acid. The aldohexose or aldohexose derivative should be at least 25% esterified, based on the total hydroxyl availability. At least about

15% of the total fatty acid in the ester is saturated fatty acid having from about 12 to about 24 carbon atoms. The remainder of the fatty acid is selected from the group consisting of "short chain" fatty acids having from 2 to about 6 carbon atoms or unsaturated "long chain" fatty acids having from about 12 to about 24 carbon atoms, the molar proportion of the said "short chain" fatty acids not substantially exceeding the total molar proportion of the said saturated and unsaturated "long chain" fatty acid.

It will be appreciated that the ester of aldohexose or of aldohexose derivative 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 aldohexose ester for this invention is glucose esterified with an average of 1½ palmitic acid groups. Other long-chain saturated fatty acid groups such as those of lauric, myristic, stearic, arachidic, behenic or lignoceric acids, and mixtures thereof, can be present in the ester in place of part or all of the palmitic acid groups. The glucose ester must be at least 25% esterified, based on the total hydroxyl availability, and be esterified with at least about 15%, based on the total fatty acid in the ester, of long-chain saturated fatty acid. Subject to this limitation, the glucose can be esterified additionally with short-chain fatty acids such as acetic, propionic, butyric, valeric, and caproic acids, or with long-chain unsaturated fatty acids such as lauroleic, myristoleic, palmitoleic, oleic, linoleic, linolenic, elaidic, gadoleic, arachidonic, erucic, brassidic, clupanodonic and/or selacholeic acids.

Other suitable aldohexoses which can be used to form esters for use in the practice of this invention are mannose and galactose. Examples of suitable aldohexose derivatives which can be similarly esterified for use in this invention are glucuronolactone, glucuronic acid, galacturonic acid, gluconolactone, mannonolactone, and methyl glucoside.

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," de-waxing, 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 preferably are removed. Base salad oils can also be formed by directed, low-temperature interesterification 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, such as acetic, 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 esters of aldohexose and aldohexose derivatives suitable for use in this invention can be prepared by a variety of known methods. For example, the aldohexose or derivatives can be reacted with mixtures of acid chlorides, or acid anhydrides, of suitable fatty acids. Aldohexose or derivatives 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 ester of aldohexose or derivative.

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 coil, 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

39.7 g. of glucose were partially esterified by reaction with 60.5 g. of palmitoyl chloride in the presence of 1750 ml. pyridine. The glucose was first dissolved in the warm pyridine and then the fatty acid chloride was slowly added thereto. The reaction mixture was allowed to stand at room temperature for about 20 hours. The solvent was then partially stripped off under high vacuum until about 250 ml. of the reaction mixture remained. The reaction mixture solution became cloudy and was then held in an ice bath and stirred until a white precipitate of about 80 g. of glucose partial palmitate was obtained. The partial ester had a hydroxyl value of 286 and an average of about 1.8 esterified hydroxyl groups per molecule (36% esterified).

When 0.01% by weight of the said glucose ester was dissolved in winterized cottonseed oil, the chill test was lengthened from 8 hours to about 24 hours.

The average degree of esterification of glucose can be controlled by varying the ratio of reactants in the procedure of this example; and when a higher glucose ester such as glucose tetrapalmitate is substituted for the glucose partial ester used in this example, substantially similar improvement in the chill test is obtained.

Example 2

Ten g. of glucose were partially esterified by reaction with 25 g. of the fatty acid chlorides of cottonseed oil (about ½ linoleoyl and about ¼ each of oleoyl and palmitoyl chlorides; these figures do not account for the presence of small amounts of several other acyl chlorides, such as stearoyl chloride, which are also known to be present) in the presence of 500 ml. pyridine. The glucose was dissolved in the warm pyridine and then the fatty acid chlorides were added slowly. This reaction mixture was allowed to stand at room temperature for about 20 hours. The pyridine was then stripped off under high vacuum with gentle heating. The resulting glucose partial ester had a hydroxyl value of 163, a saponification value of 274, and an average of about 2.7 esterified hydroxyl groups per molecule (54% esterified).

0.05% by weight of the glucose ester dissolved in winterized cottonseed oil lengthened the chill test from 8 hours to about 49 hours.

When equimolar portions of mannose and galactose are substituted for glucose in this example, substantially similar improvement in chill test results are obtained.

Example 3

33 g. of methyl glucoside were partially esterified by reaction with 70 g. of palmitoyl chloride in the presence of 1000 ml. pyridine. The methyl glucoside was first dissolved in the pyridine and then the fatty acid chloride was added slowly. The solvent was removed under a high vacuum at an elevated temperature. After several water washings, 62 g. of the methyl glucoside partial palmitate product had a hydroxyl value of 149, an acid value of 22, and an average between 1 and 2 esterified hydroxyl groups per molecule.

0.01% by weight of the methyl glucoside ester dissolved in winterized cottonseed oil lengthened the chill test from 8 hours to about 24 hours.

Other long chain fatty acid esters of glucose, methyl glucoside, glucuronolactone, glucuronic acid, and gluconolactone and the corresponding esters of the stereoisomeric aldohexoses and aldohexose derivatives which show excellent crystal inhibiting activity can be prepared by various methods including the methods described in Examples 1–3 above, and may be similarly admixed with base oil to provide comparable improvement when subjected to the chill test. The following examples will serve to illustrate the crystal inhibiting activity with several of these esters.

Example 4

Solution in winterized cottonseed oil of 0.005% by weight of glucono-delta-lactone ester having an average between one and two palmitoyl groups per molecule lengthened the chill test from 8 to about 24 hours. Similar results were obtained with 0.1% of the same ester in said oil.

Example 5

Solution of 0.1% by weight of methylglucoside distearate in winterized cottonseed oil lengthened the chill test from 8 hours to greater than 16 hours.

Example 6

Solution of 0.01% by weight of glucuronolacetone monopalmitate in winterized cottonseed oil lengthened the chill test from 8 hours to about 40 hours.

When galacturonic acid is substituted for glucuronolactone in this example, substantially similar improvement in chill test results is obtained.

Example 7

Solution in winterized cottonseed oil of 0.1% by weight of glucono-delta-lacetone ester having an average between three and four palmitoyl groups per molecule lengthened the chill test from 8 to about 41 hours.

Example 8

Solution in refined, bleached soybean oil of 0.01% by weight of glucono-delta-lactone ester having an average between three and four palmitoyl groups per molecule lengthened the chill test from 5½ hours to about 30 hours. When the concentration of the ester used in another portion of the oil was increased to about 0.1%, the chill test was lengthened from about 5½ hours to about 23½ hours.

The following example illustrates one of the combined long and short chain fatty esters of glucose herein described which show the excellent crystal inhibiting activity of this invention.

Example 9

Solution of 0.1% by weight of diacetyl tripalmitoyl glucose in a sample of winterized cottonseed oil lengthened the chill test from 8 hours to about 60 hours.

When winterized corn oil is substituted for winterized cottonseed oil in this example, substantially similar improvement in the chill test is obtained.

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 molecule

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 generally tend to be intermediate in their effect on inhibition action. Under certain conditions, however, the cis- and trans-chains may 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. Amounts of ester in excess of about 0.5%, by weight, are unnecessary as affording no significant added improvement of the oil.

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 a crystal inhibiting amount and at least about 0.001%, by weight, of fatty acid ester of monosaccharidic material having an oxide ring structure and selected from the group consisting of aldohexose, aldohexuronolactone, aldohexuronic acid, aldohexonolactone, and methyl aldohexoside, the said material being at least 25% esterified, based on the total hydroxyl availability, with at least about 15%, based on the total fatty acid in the ester, of saturated long chain fatty acid having from about 12 to about 24 carbon atoms, the balance of the fatty acid being selected from the group consisting of short chain fatty acids having from 2 to about 6 carbon atoms and unsaturated long chain fatty acids having from about 12 to about 24 carbon atoms, the molar proportion of the said short chain fatty acids not substantially exceeding the total molar proportion of the said saturated and unsaturated long chain fatty acids.

2. A salad oil according to claim **1** wherein the monosaccharidic moiety of the ester is derived from glucose.

3. A salad oil according to claim **1** wherein the fatty acid groups consist essentially of palmitic acid groups.

4. A salad oil according to claim **1** wherein the fatty acid groups consist essentially of stearic acid groups.

5. A salad oil according to claim **1** wherein the fatty acid groups consist essentially of acetic and palmitic acid groups.

6. A salad oil according to claim **1** wherein the fatty acid groups comprise linoleic, oleic, and palmitic acid groups.

7. A clear glyceride salad oil having superior resistance to deposition of high-melting solids and comprising winterized cottonseed oil having dissolved therein about 0.1%, by weight, of methylglucoside distearate.

8. A clear glyceride salad oil having superior resistance to deposition of high-melting solids and comprising winterized cottonseed oil having dissolved therein about 0.1%, by weight, of glucono-delta-lactone ester having an average of between three and four palmitoyl groups per molecule.

9. A clear glyceride salad oil having superior resistance to deposition of high-melting solids and comprising winterized cottonseed oil having dissolved therein about 0.1%, by weight, of diacetyl tripalmitoyl glucose.

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A. LOUIS MONACELL, *Primary Examiner.*