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LIQUID SHORTENING

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This invention relates to a novel shortening composition. More particularly, this invention relates to a liquid shortening made from edible oils which is capable of producing excellent quality, high volume cakes.

Substantially all shortenings in general use today are glycerides in one form or another. Although the naturally-occurring liquid triglyceride oils have been used to some extent as "shortening," they have in general been found to be unsatisfactory for shortening purposes in the absence of further treatment. It has been the more usual practice to hydrogenate or harden liquid triglyceride oils with the result that the plastic or solid shortenings are the most common type available in the market today. These plastic shortenings usually contain small amounts of emulsifiers and modifiers of various kinds, such as the mono- and diglycerides of higher fatty acids, which impart "high ratio" and other desirable properties to shortening and provide good cake performance in terms of volume, texture and tenderness.

Since the usual plastic shortenings are not fluid or pourable at ordinary temperatures, difficulty is encountered in dispensing, measuring, and mixing them with other substances. It has been recognized that certain advantages reside in the use of liquid shortenings over the plastic shortenings in ease of handling, measurement, and other usage. However, the conventional plastic shortening emulsifiers have been found to be deficient in their ability to produce stable cake batters and cakes of high volume when used in a fluid or liquid shortening system.

Accordingly, it is the primary object of this invention to provide a novel liquid shortening which is capable of producing stable cake batters and baked cakes of enhanced volumes.

In accordance with this invention it has been found that enhanced cake batter stability and improved cake volumes are obtained with a liquid shortening comprising a normally liquid glyceride base oil containing from about 0.1% to about 4% of an alkenyl substituted cyclic dicarboxylic acid anhydride having from about 4 to 5 carbon atoms in the dicarboxylic acid anhydride portion of the molecule and from about 12 to about 22 carbon atoms in the alkenyl radical, and from about 1.5% to about 24% of an alpha-phase crystal-tending emulsifier containing at least one higher fatty acid radical having from about 12 to about 22 carbon atoms and at least one free and unesterified hydroxyl group. All percentages mentioned herein are by weight of the shortening unless otherwise stated.

The base oil of the fluid shortening of this invention is a normally liquid triglyceride. Suitable base oils for this shortening can be derived from animal, vegetable, or marine sources including naturally-occurring liquid triglyceride oils such as cottonseed oil, soybean oil, rapeseed oil, safflower oil, sesame seed oil, sunflower see oil, and sardine oil. Also, suitable liquid oil fractions can be obtained from palm oil, lard, and tallow, as for example, by fractional crystallization or interesterification

with simultaneous crystallization of insoluble glycerides, followed by separation of the liquid oil fraction. Oils predominating in glycerides of unsaturated acids may require partial hydrogenation to maintain flavor. Refined cottonseed oil and refined and partially hydrogenated soybean oil (iodine value of about 110±10) have been found to be very suitable for use as glyceride base oils of this invention.

The alkenyl substituted dicarboxylic acid anhydrides of this invention are the cyclic anhydrides of dicarboxylic acids having from about 4 to 5 carbon atoms in which one of the hydrogens attached to an alpha carbon relative to the functional anhydride group is substituted with an alkenyl radical having from about 12 to about 22 carbon atoms. Included among the alkenyl substituted dicarboxylic acid anhydrides of this invention are the tetradecenyl, octadecenyl, and docosenyl substituted succinic and glutaric acid anhydrides. These compounds can be prepared by various means which are known to those skilled in the art; for example, by the reaction of monoolefin with unsaturated dicarboxylic acid anhydride at elevated temperatures. In particular, octadecenyl succinic anhydride can be prepared by reaction of 1-octadecene with maleic anhydride at elevated temperatures by methods described in U.S. Patent 2,411,215, granted to Kise and Engle, November 11, 1946, and U.S. Patent 2,561,232, granted to Rudel and Wasson, July 17, 1951.

The alpha-phase crystal-tending emulsifiers of this invention are both lipophilic and hydrophilic and contain in the molecule at least one higher fatty acid radical having from about 12 to about 22 carbon atoms and at least one free and unesterified hydroxyl group. Said emulsifiers are characterized by their tendency to crystallize in an alpha-phase rather than a beta- or beta-prime phase. These types of polymorphic crystalline structures can be identified by their X-ray diffraction patterns and are described in U.S. Patents 2,521,241–2, granted to Mitchell, September 5, 1950. The alpha-phase crystalline form is the least stable, least dense, and lowest melting of these crystalline forms.

Although it is not desired to be bound by any particular theory, it is believed that the film-forming tendency of the alpha-phase crystal-tending emulsifier promotes the incorporation of air during the preparation of a shortening containing emulsion, such as a cake batter. The incorporation of air in a cake batter is achieved essentially by the production of a foam through an extension of the protein film. However, the oily phase of the batter normally tends to hinder the foam building properties of the protein. It is believed that the film-forming tendency of the alpha-phase crystal-tending emulsifier at the oil-aqueous phase interface prevents the oily phase from acting as a foam depressant toward the protein.

Among the alpha-phase crystal-tending emulsifiers that can be used in the practice of this invention are the following classes of materials which are set forth by way of example only, and the invention is not to be limited to these specific alpha-phase crystal-tending emulsifiers:

(a) A monoester of a straight chain aliphatic diol with a saturated fatty acid, said diol containing from 3 to 5 carbon atoms and said saturated fatty acid containing from about 14 to about 22 carbon atoms;

(b) The condensation product of a monohydroxy-monocarboxylic acid having from 2 to 6 carbon atoms with

a partial fatty acid glyceride containing an average of from 1 to 2 fatty acid radicals having from about 14 to about 22 carbon atoms;

(c) A 1,3-diglyceride containing a saturated fatty acid radical having from about 16 to about 22 carbon atoms and a saturated fatty acid radical having from 2 to 4 carbon atoms;

(d) A 1,2-diglyceride containing a saturated fatty acid radical having from about 16 to about 22 carbon atoms and a saturated fatty acid radical having from 12 to 18 carbon atoms; and

(e) A saturated fatty acid ester of diethylene glycol, said fatty acid having from about 14 to about 22 carbon atoms.

The foregoing classes of alpha-phase crystal-tending emulsifiers are illustrated in greater detail, including typical methods of preparation, in the material that follows hereinafter. For example, the above-mentioned diol monoesters of fatty acids which can be employed in this invention include: propylene glycol monostearate; 1,3-propanediol monostearate; 1,4-butanediol monostearate; 1,3-butanediol monostearate; 1,5-pentanediol monostearate; and the corresponding monoesters of the preceding-named diols with myristic acid, palmitic acid, arachidic acid, and behenic acid. The said diol monoesters can be prepared by direct esterification or interesterification of the diol by reaction with the desired fatty acid or a fatty ester of a monohydric or polyhydric alcohol under appropriate conditions of temperature, either with or without catalyst and/or solvent. In the direct reactions between fatty acid and diol, the reactants are normally mixed in ratios of 1 mole of fatty acid to .75 or more moles of diol. The yield of monoester is enhanced by using solvents such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, xylene, or toluene; and catalysts such as p-toluene sulfonic acid, sulfuric acid, hydrogen chloride, or zinc chloride and other acidic or salt types are particularly effective in accelerating the rate of esterification.

Interesterification of the diol with fatty esters of alcohols such as methanol, ethanol, and propanol as well as fatty esters of polyhydric alcohols such as glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, glycerol, erythritol, ribitol, sorbitol, mannitol, and others is a particularly good path to the diol monoesters. Mutual solvents are of good value including such solvents as dimethylformamide, dimethylacetamide, dimethylsulfoxide, dioxane, pyridine, xylene, and toluene. Catalysts of greatest value are such catalysts as sodium methoxide, benzyl trimethyl ammonium methoxide, sodium hydroxide and others described by Eckey, U.S. Patent 2,442,532, at column 24, line 18 et seq.

The reaction products produced by interesterification and containing diol monoester can be recovered by inactivation of the catalyst with an appropriate acid such as acetic or phosphoric acid. The reaction products can be freed of solvents by distillation and used as prepared, or they can be purified by water washing and crystallization techniques to further enrich the diol monoester content. Crystallization from an aliphatic hydrocarbon solvent such as hexane is particularly effective in enriching the monoester in the crystalline phase. Solvent partition methods are also highly effective in concentrating the diol monoesters.

Among the above-mentioned monohydroxy-monocarboxylic acid esters of partial fatty acid glycerides which are suitable alpha-phase crystal-tending emulsifiers in the practice of this invention are the condensation products of glycolic acid, lactic acid, sarcolactic acid, hydracrylic acid, 4-hydroxybutyric acid, 5-hydroxypentanoic acid, and 6-hydroxyhexanoic acid with partial glycerides containing at least one acyl radical derived from one or more of the hereinbefore-described "long-chain" fatty acids, i.e., myristic, palmitic, stearic, arachidic and behenic acids. Unsaturated acids such, for example, as oleic and linoleic acids also can be present in the condensation product. The partial fatty acid glycerides used to prepare said condensation products can be either pure esters of fatty acids having from about 14 to about 22 carbon atoms, or mixtures of fatty acid esters containing such fatty acid radicals. They are commonly made by reacting a triglyceride oil or fat, for example, cottonseed oil or soybean oil, with glycerine in the presence of a catalyst, usually an alkaline catalyst such as sodium hydroxide. U.S. Patents 2,206,167–8, granted to Edeler and Richardson, July 2, 1940, describe typical procedures for making edible monoglycerides and diglycerides. These materials contain on the order of 45% to 60% monoglyceride, the balance comprising diglyceride and a smaller percentage of triglycerides. The so-called "distilled" monoglyceride products which are characterized by having a higher monoglyceride content, commonly of the order of 90% or more, can also be used to form suitable esters with monohydroxy-monocarboxylic acid in accordance with this invention. Such products are marketed under the trademark "Myverol" and methods of manufacture thereof are described in U.S. Patents 2,634,278–9; 2,701,769; and 2,727,913.

The monohydroxy-monocarboxylic acid esters of partial fatty acid glycerides can be prepared by esterification of the mono- and diglycerides with the monohydroxy-monocarboxylic acid under partial vacuum and elevated temperatures. For example, lactic acid and mono- and diglycerides of substantially completely hydrogenated soybean oil can be esterified under partial vacuum and elevated temperatures of approximately 300° F. They also can be prepared by reacting glycerine, fatty acid, and monohydroxy-monocarboxylic acid. Another example of a method of preparation is described in U.S. Patent 2,690,971, granted to Iveson et al., October 5, 1954.

The hereinbefore defined 1,3-diglycerides can be prepared by: (1) partial acylation of a long chain monoglyceride with either the desired short chain acid, its acid chloride, or its acid anhydride under conditions known to those skilled in the art; (2) partial acylation of a short chain monoglyceride with either the desired long chain acid, its acid chloride, or its acid anhydride under conditions well known to those skilled in the art; and (3) interesterification of appropriate mixtures of long chain monoglycerides, diglycerides and/or triglycerides with short chain monoglycerides, diglycerides, and/or triglycerides, either with or without added glycerol under conditions such that the resulting reactant composition will contain approximately one equivalent of long-chain acyl component, one equivalent of short chain acyl component, and one mole of glycerol. This reaction is effectively catalyzed by basic catalysts such as sodium methoxide, quaternary ammonium bases and other catalysts such as those taught by Eckey in U.S. Patent 2,442,532, at column 24, line 18 et seq.

The crude reaction products containing substantial amounts of the desired 1,3-diglycerides can be used as prepared or the desired diglyceride component can be concentrated by application of appropriate methods of fractionation such as molecular distillation, fractional crystallization, and/or solvent partition. The crude 1,3-diglyceride reaction product which is used can contain the isomeric 1,2-diglyceride which is formed during the preparation of the 1,3-diglyceride.

The hereinbefore defined 1,2-diglycerides can be obtained by several routes. (1) They are the relatively lower-melting components of superglycerinated, hydrogenated fats and can be isolated by crystallization fractionation. Crystallization fractionation of a superglycerinated, hydrogenated soybean oil in an aliphatic hydrocarbon solvent such as hexane leads to isolation of 1,2-distearin in a 15% yield in a purity of from about 80% to 90%. (2) Thermal isomerization by the meth-

od of A. Crossley et al., J. Chem. Soc., p. 700 (1959), of a pure 1,3-diglyceride prepared by the method of U.S. Patent 2,626,952, Lange and Baur, leads to an equilibrium mixture of 1,2- and 1,3-diglycerides in which the 1,2-diglyceride is 40% of the mixture. The desired 1,2-diglyceride is easily isolated by the fractional crystallization procedure described by A. Crossley in the previously mentioned journal article. (3) Other methods of isomerizing 1,3-diglyceride to an equilibrium mixture with 1,2-diglycerides, such as an acid or base catalyzed isomerization, are equally as advantageous to the preparation of 1,2-diglycerides, yielding mixtures which may be fractionated by crystallization. (4) Specific synthesis can be accomplished by partial acylation of a 2-monoglyceride to yield a mixture of 2-monoglyceride, 1-acyl-2-monoglyceride and 1,3-diacyl-2-monoglyceride. The 1-acyl-2-monoglyceride is separable from this product by fractional crystallization as the desired 1,2-diglyceride. (5) Specific synthesis also can be accomplished by diacylation of a glycerol derivative blocked at a primary hydroxy position. The blocking group is eliminated in a manner such as to yield the diacylated glycerol with the acyl groups in the 1,2-positions. Glycerol derivatives amenable to this type of synthesis include 1-triphenylmethyl glycerol ether, 1-benzyl glycerol ether, and 1-tetrahydropyranyl glycerol ether. The triphenyl methyl and benzyl groups are removed by hydrogenolysis and the tetrahydropyranyl group is removed by boration with boric acid or alkoxy boric acids followed by aqueous hydrolysis of the borate intermediate.

The hereinbefore defined esters of diethylene glycol and long-chain saturated fatty acids can be prepared by the same procedures used to prepare the above-mentioned monoesters of straight chain aliphatic diols with said fatty acids, using diethylene glycol in place of said diols.

Although specific methods of preparing the aforesaid additives have been described herein, it is not intended that the invention should be limited to any particular method of preparation of these materials.

It has been found that the herein-described combination of from about 0.1% to about 4% alkenyl substituted dicarboxylic acid anhydride and from about 1.5% to about 24%, preferably between 1.5% and 16%, alpha-phase crystal-tending emulsifier in a liquid glyceride oil provides a stable liquid shortening which is particularly advantageous for the preparation of stable cake batters which yield high volume cakes.

All types of cakes can be made with the fluid shortening of this invention. White cakes, yellow cakes, chocolate cakes, pound cakes, and many other cakes of excellent quality can be prepared simply by mixing the shortening of this invention with the other ingredients of the cake in a single mixing step. Although specific types of cakes have been mentioned, this should in no way be held to limit the invention to the preparation of any specific cake.

The acid anhydride and the alpha-phase crystal-tending emulsifier additives of this invention can be incorporated in the shortening by mixing them into the liquid glyceride base oil. It is preferable to form a solution of the additives in the liquid oily phase and this may require elevation of temperature and/or prolonged holding times to dissolve the additive.

The liquid shortening of this invention can also contain small amounts (usually not exceeding about 8% by weight of the shortening) of conventional emulsifiers and other agents such, for example, as fatty acid mono- and diglyceride emulsifiers, sorbitan and polyoxyethylene sorbitan esters of higher fatty acids, lactic and/or citric acid esters of mono- and/or diglycerides or of other higher fatty acid-containing polyol partial esters, free fatty acids, and many other substances commonly used in shortenings to improve their cooking or other properties.

Various minor ingredients such as: flavor; color; antioxidants, such as butylated hydroxytoluene, butylated hydroxyanisole, citric acid, and methyl silicone; and mold inhibitors, such as sorbic acid and sodium benzoate can also be added to the compositions of this invention if desired.

The following example describes a specific embodiment of the invention and is set forth for purposes of illustration, and not limitation, of the invention described herein.

Example

A stable fluid shortening was prepared by mixing together with slight warming the following materials in the stated amounts:

	Percent by weight
Refined and bleached cottonseed oil	85.75
Propylene glycol stearate (approximately ½ each mono- and diesters)	14.00
Octadecenyl succinic anhydride	0.25

The above fluid shortening was used to prepare an excellent single-stage batter-mixed high ratio white cake consisting of the following ingredients:

	Parts by weight, g.
Cake flour	107.0
Granulated sugar	133.0
Sodium chloride	2.5
Double-acting baking powder	6.8
Shortening	47.5
Whole milk	130.0
Egg whites (fresh)	60.0

The fluid shortening and the other liquid ingredients (milk and egg whites) were added simultaneously to all of the dry mix ingredients and mixed with a Sunbeam table model electric mixer at 500 r.p.m. for a total of 4 minutes. 400 g. of batter was placed in an 8-inch pan and baked in an oven at 365° F. for about 25 minutes.

Three other cakes were baked according to the above procedure using shortenings which contained various other quantities of octadecenyl succinic anhydride in place of the 0.25% used above. The increase in the amount of anhydride used was offset by a complementary decrease in the amount of base oil used. The table set forth below shows the hot and cold cake volumes obtained by the use of these improved shortenings. All cake volumes are stated in cc. per 400 g. of batter. The hot volumes were measured immediately after completion of the 25 minute baking period; and the cold volumes were measured after standing at room temperature for 20 minutes. The cakes containing octadecenyl succinic anhydride had excellent volume as shown in the table below.

Percent anhydride (shortening weight basis):	Hot/cold cake vol. (cc./400 g. batter)
0.25	1385/1260
0.50	1490/1370
1.00	1490/1385
2.00	1650/1555
Control cake without anhydride	*/840

*Not determined.

Excellent cakes of comparable volume and eating quality are obtained when equal weights of alpha-phase crystal-tending emulsifiers—lactyl monobehenin, 1-acetyl-3-monostearin, 1,2-distearin, and diethylene glycol monolaurate—are substituted for the 7.0% propylene glycol monostearate in the above specific example.

When equivalent weights of tetradecenyl glutaric anhydride and docosenyl succinic anhydride are substituted for the octadecenyl succinic anhydride in formulations of the above example, substantially similar excellent high volume cakes are obtained.

When peanut oil, rapeseed oil, and soybean oil are substituted for the cottonseed oil in the above example, and the combination of 4% octadecenyl succinic anhydride and 16% propylene glycol monostearate is substituted for the combination of 0.25% octadecenyl suc-

cinic anhydride and 7% propylene glycol monostearate in the above example, substantially similar fluid shortenings are obtained which have the excellent cake baking properties described herein.

The cake enhancing properties of the alkenyl substituted cyclic dicarboxylic acid anhydrides in the liquid shortening of this invention suggests that the alkyl analogs of said anhydrides also can be used as cake enhancers in the liquid shortening of this invention.

What is claimed is:

1. A liquid shortening which comprises a normally liquid glyceride base oil containing, by weight of the shortening, from about 0.1% to about 4% alkenyl substituted cyclic dicarboxylic acid anhydride having from about 4 to 5 carbon atoms in the dicarboxylic acid anhydride portion of the molecule and from about 12 to about 22 carbon atoms in the alkenyl radical and from about 1.5% to about 24% alpha-phase crystal-tending emulsifier containing at least one higher fatty acid radical having from about 12 to about 22 carbon atoms and at least one free and unesterified hydroxyl group.

2. The composition of claim **1** in which the alpha-phase crystal-tending emulsifier is present in an amount between 1.5% and 16%.

3. The composition of claim **1** in which the normally liquid glyceride base oil is cottonseed oil.

4. The composition of claim **1** in which the alkenyl substituted dicarboxylic acid anhydride is octadecenyl succinic anhydride.

5. The composition of claim **1** in which the alpha-phase crystal-tending emulsifier is selected from the group consisting of

(a) a monoester of a straight chain aliphatic diol with a saturated fatty acid, said diol containing from 3 to 5 carbon atoms and said saturated fatty acid containing from about 14 to about 22 carbon atoms;

(b) the condensation product of a monohydroxy-monocarboxylic acid having from 2 to 6 carbon atoms with a partial fatty acid glyceride containing an average of from 1 to 2 fatty acid radicals having from about 14 to about 22 carbon atoms;

(c) a 1,3-diglyceride containing a saturated fatty acid radical having from about 16 to about 22 carbon atoms and a saturated fatty acid radical having from 2 to 4 carbon atoms;

(d) a 1,2-diglyceride containing a saturated fatty acid radical having from about 16 to about 22 carbon atoms and a saturated fatty acid radical having from 12 to 18 carbon atoms; and

(e) a saturated fatty acid ester of diethylene glycol, said fatty acid having from about 14 to about 22 carbon atoms.

6. The composition of claim **5** in which the alpha-phase crystal-tending emulsifier is propylene glycol monostearate.

7. The composition of claim **5** in which the alkenyl substituted dicarboxylic acid anhydride is octadecenyl succinic anhydride.

8. A liquid shortening which comprises a normally liquid glyceride base oil containing, by weight of the shortening, from about 0.1% to about 4% octadecenyl succinic anhydride and from about 1.5% to about 16% propylene glycol monostearate.

9. The composition of claim **8** in which the normally liquid glyceride base oil is cottonseed oil.

10. The method of improving the volume of cakes which comprises incorporating in the cake a liquid shortening comprising a liquid glyceride base oil containing, by weight of the shortening, from about 0.1% to about 4% alkenyl substituted cyclic dicarboxylic acid anhydride having from about 4 to 5 carbon atoms in the dicarboxylic acid anhydride portion of the molecule and from about 12 to about 22 carbon atoms in the alkenyl radical and from about 1.5% to about 24% alpha-phase crystal-tending emulsifier containing at least one higher fatty acid radical having from about 12 to about 22 carbon atoms and at least one free and unesterified hydroxyl group.

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