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GLYCERIDIC OIL COMPOSITIONS AND METHOD OF PRODUCING SAME

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This application is a continuation in part of the copending applications, S. N. 608,101, filed July 31, 1945, now Patent No. 2,485,631; S. N. 608,102, filed July 31, 1945, now Patent No. 2,485,632; and S. N. 608,380, filed August 1, 1945, now Patent No. 2,485,633.

This invention relates to glyceridic oil compositions, and more particularly to glyceridic oil compositions possessing marked resistance to deterioration.

An object of this invention is to retard the deterioration of glyceridic oils and more particularly hydrogenated and deodorized glyceridic oils.

Another object of this invention is to provide valuable surface acting effects in glyceridic oils, such as the prevention of the exudation of moisture from emulsions containing glyceridic oils.

Another object of this invention is to incorporate agents in glyceridic oils, which agents markedly retard deterioration of glyceridic oils, but due to their insolubility or immiscibility per se in glyceridic oils, are difficult to incorporate therein.

It is well recognized that glyceridic oils and fats develop rancidity under a variety of conditions. Rancidity renders their use, especially for edible products, undesirable and, in some cases, entirely unsatisfactory. Various materials have been heretofore proposed for retarding the development of rancidity in glyceridic oils and fats, but frequently these materials are substantially incompatible with oils and fats, and in some cases their efficacy is questionable.

In accordance with this invention, compositions comprising principally glyceridic oils or a mixture of glyceridic oils are produced which do not develop rancidity over a relatively prolonged period. These compositions comprise a glyceridic oil or a plurality of glyceridic oils and a mono-alkyl, mono-alkylene, di-alkyl or di-alkylene ester of a simple functional aliphatic poly-carboxylic acid containing at least three carboxyl groups or of an hydroxy aliphatic poly-carboxylic acid containing at least three carboxyl groups and no functional groupings other than the hydroxyl and carboxyl groups. The primary ionization constant of the simple functional poly-carboxylic acid or the hydroxy aliphatic poly-carboxylic acid is within the range of 1.0×10^{-2} and 1.0×10^{-4}, and preferably 1.7×10^{-3} and 1.0×10^{-4}, at 25° C.

With some glyceridic oils, the addition of such di-alkyl or di-alkylene esters retards the development of rancidity. The mono-alkyl and mono-alkylene esters, however, improve to a markedly greater degree the retardation of rancidity than

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do the di-alkyl and di-alkylene esters. In fact, a much greater amount of such di-alkyl and di-alkylene esters must be employed to effect the same retardation of rancidity. However, as later discussed in more detail, when incorporated in a glyceridic oil which is employed as a component in an edible oil-water system such as margarine, butter or cheese, the di-alkyl and di-alkylene esters prevent the exudation of moisture from such systems.

In some cases, the mono-alkyl or mono-alkylene ester is not soluble or miscible to a sufficient degree in the glyceridic oil to produce a substantially homogeneous composition. To disperse such mono-alkyl or mono-alkylene ester throughout the glyceridic oil, an oil-soluble hydrophilic coupling or solubilizing agent is employed. Examples of satisfactory solubilizing agents for this purpose are unsubstituted mono-hydric aliphatic alcohols having at least 6 carbon atoms, mono-carboxylic acids having at least 10 carbon atoms and mono-carboxylic acid mono-esters of glycerol or propylene glycol or their polymers, in which the mono-carboxylic acid residue has at least 10 carbon atoms. When an oil-soluble hydrophilic coupling or solubilizing agent is employed, the mono-ester is first dissolved in such agent and the resulting mixture is incorporated in the glyceridic oil.

The compositions of this invention may be substantially all oil systems, such as shortening, or aqueous and oil systems, such as margarine. Some glyceridic oils which are initially in an all oil system are later utilized in an oil-water system. For example, shortening, while initially an all oil system, is employed as a component in batter and its ability to emulsify with water is of paramount importance. By adding a sufficient quantity of mono- and/or di-esters of the poly-carboxylic acids and a suitable quantity of the hydrophilic coupling agent, a shortening, for example, is obtained which when utilized as a component in baking has a relatively high lift characteristic, permits a high ratio of sugar to flour and produces a resulting baked product which is substantially homogeneous and has a fine texture. In addition, such shortening markedly facilitates the mixing of the water phase components of the batter such as milk, and the resulting batter is materially less viscous than batter prepared from ordinary shortening. Certain mono- and/or di-esters of poly-carboxylic acids alone or in combination with a hydrophilic coupling or solubilizing agent, such as mono-glycerides of a fatty acid in which the fatty acid has at least 10 car-

bon atoms, have been found to have marked emulsifying effect.

Glyceridic oil containing the di-alkyl or di-alkylene esters of the simple functional poly-carboxylic acid or the hydroxy poly-carboxylic acid are especially adapted for use in margarine, and margarine produced with such glyceridic oils has marked moisture retaining properties and does not manifest the so-called leakage or weeping. The concentration of the di-alkyl or di-alkylene ester in the glyceridic oil employed for use in margarine may vary over wide limits depending upon inter alia the amount of milk moisture in the margarine emulsion in which the glyceridic oil is used, the method of chilling the margarine and the apparatus employed for the processing of the margarine; but a concentration of .06 to 1.9% by weight of the di-ester in the glyceridic oil is satisfactory, although for some purposes as much as 4% or higher of the di-ester may be used. Desirably, the alkyl group of such di-alkyl esters used for this purpose has at least 12 carbon atoms, and the alkylene group of such di-alkylene ester has at least 16 carbon atoms. The preferred concentration of the di-alkyl ester in the glyceridic oil for use in margarine is .25 to .6% by weight of the ester in the glyceridic oil when the alkyl group in the ester has from 8 to 16 carbon atoms, and .1 to .3% by weight of the ester in the glyceridic oil when the alkyl group has at least 16 carbon atoms. The preferred concentration of such di-alkylene ester is .3 to .6% by weight of the glyceridic oil and desirably the alkylene group of such di-alkylene ester has at least 16 carbon atoms.

The amount of mono-alkyl or mono-alkylene esters of the simple functional aliphatic poly-carboxylic acids or the hydroxy poly-carboxylic acids which is incorporated in the glyceridic oil may vary over wide limits depending upon the particular use of the glyceridic oils. For example, if it is fundamentally desired to retard the rancidity of the glyceridic oil, concentrations of .002 to 1% by weight, and preferably .01 to .1% by weight, of the mono-alkyl or mono-alkylene esters may be used. On the other hand, if the glyceridic oil is to be utilized as a shortening of the so-called high ratio type which permits a high ratio of sugar to flour .5 to 4% or even as high as 10%, and preferably .5 to 2% by weight of the mono-alkyl or mono-alkylene ester may be advantageously used.

Conveniently, if both the mono- and di-esters of the poly-carboxylic acid are to be incorporated in the glyceridic oil, the mono-ester and di-ester may be prepared simultaneously. This simultaneous production of mono- and the corresponding di-esters of the poly-carboxylic acid can be achieved by reacting the required amount of the poly-carboxylic acid with a primary or secondary alkyl or alkylene alcohol to produce the desired amount of the mono-ester together with an amount of the corresponding di-ester of the poly-carboxylic acid.

In the copending applications, S. N. 608,101, S. N. 608,102 and S. N. 608,380, which issued as Patents Nos. 2,485,631, 2,485,632 and 2,485,633, respectively, comparative tests are described which demonstrate that certain mono-esters of a poly-carboxylic acid, such as mono-esters of citric acid, when incorporated in glyceridic oils markedly retard deterioration of such oils. For example, mono-stearyl citrate, when incorporated in corn salad oil, is capable of retarding materially the development of rancidity of the oil as indicated by peroxide number determinations. On the other hand, certain di-esters of poly-carboxylic acids, such as the di-esters of citric acid, when incorporated in the glyceridic oil utilized in the production of margarine, materially improve the moisture retention characteristics as described in the copending application S. N. 747,848, filed May 13, 1947, now Patent No. 2,485,634. The mono-alkyl or mono-alkylene esters of simple functional aliphatic poly-carboxylic acids having at least three carboxyl groups and of hydroxy aliphatic poly-carboxylic acids containing at least three carboxyl groups and having no functional groupings other than the hydroxyl and carboxyl groups, the primary ionization constants of the polycarboxylic acids being within the range of 1.0×10^{-2} and 1.0×10^{-4} at 25° C., also manifest the same characteristics as the mono-alkyl and mono-alkylene esters of citric acid described in these copending applications. Likewise, the di-alkyl and di-alkylene esters of these poly-carboxylic acids also effect similar results when incorporated in glyceridic oil as do the di-alkyl and di-alkylene esters of citric acid.

The mono-alkyl, mono-alkylene, di-alkyl or di-alkylene ester of the poly-carboxylic acid, or mixtures of such esters, may be incorporated in the oil directly or may be added in the form of a solution in an oil-coupling or solubilizing agent. It is particularly advantageous to utilize the solution of the esters in the oil-coupling or solubilizing agent when a mono-alkyl or mono-alkylene ester of the poly-carboxylic acid having less than 10 carbon atoms is desired to be incorporated in the glyceridic oil, since these latter type esters dissolve in the glyceridic oil to a very limited extent. While the oil may be heated to dissolve some of these mono-esters, such heating, particularly if a high temperature is required, materially damages the oil for some purposes. However, they may be very effectively dispersed throughout the oil if the esters are initially dissolved in the oil-coupling or solubilizing agent.

Since both the di-alkyl or di-alkylene esters of the poly-carboxylic acid and the mono-alkyl or mono-alkylene esters of the poly-carboxylic acid are desirably incorporated in the glyceridic oil, it is advantageous to prepare a mixture of the mono- and di-esters of the poly-carboxylic acid simultaneously. The mixture of mono- and di-esters of the poly-carboxylic acid may be prepared by the esterification of the poly-carboxylic acid and an alcohol, such as a mono-hydric primary or secondary alkyl or alkylene alcohol, preferably, by reacting the poly-carboxylic acid and the alcohol in proportions which favor the formation of the mono- and di-ester in the ratio desired in the mixture. The esterification may be conducted by any of the well known methods employed for the production of esters. If, however, either the mono-ester alone or the di-ester alone is desired, the reaction product of the poly-carboxylic acid and the alcohol may be purified to isolate by fractional crystallization and selective extraction the mono-ester or di-ester.

Mixtures of mono-alkyl or mono-alkylene esters of the poly-carboxylic acid or mixtures of the di-alkyl or di-alkylene esters of the poly-carboxylic acid may be incorporated in the glyceridic oil. For example, a mixture of different mono-alkyl esters of one or a plurality of the poly-carboxylic acids may be added to the glyceridic oil, or again, different di-alkylene esters of one or a plurality of the poly-carboxylic acids may be added to the glyceridic oil, or a mixture

of a mono-alkyl ester and a mono-alkylene ester of the same or different poly-carboxylic acids may be used. Again, mixtures of various solubilizing agents may be utilized to effect uniform dispersion of the esters of the poly-carboxylic acids, and particularly the mono-ester of these acids, throughout the glyceridic oil. For example, a mixture of lauryl alcohol and cetyl alcohol may be employed to effect the solubilizing of mono-isopropyl citrate in the glyceridic oil. Alternately, a mixture of different mono-acyl glycerides may be utilized for the solubilizing of the mono-ester of the poly-carboxylic acid.

Examples of the mono- and di-esters of the poly-carboxylic acids which may be incorporated in the glyceridic oil are the mono- and di-esters of those acids of the following alcohols: ethanol, propanols, octanols, decanols, dodecanols, hexadecanols, octadecanols, cosanols, docosanols, octenols, decenols, dodecenols, hexadecenols, octadecenols, cosenols and docosenols.

Examples of the poly-carboxylic acids of this invention are citric, isocitric, aconitic, dimalonic, methylenedimalonic, lactoisocitric, α,α'-di-carboxyadipic, β-carboxytricarballylic, and tricarballylic acids.

Examples of the mono-carboxylic acid mono-esters of glycerol or propylene glycol or their polymers which may be employed as solubilizing or oil-coupling agents are the mono-stearyl glycerides, mono-oleyl glycerides, mono-lauryl glycerides and mono-palmityl glycerides, or their corresponding poly-glycerol esters or mixtures thereof. These mono-carboxylic acid mono-esters, as commercially prepared, contain substantial amounts of the corresponding mono-carboxylic acid di-esters and small amounts of the corresponding mono-carbcxylic acid tri-esters. Such mono-carboxylic acid mono-esters as commercially prepared may be employed as the solubilizing agents in the compositions of this invention. Mono-glycerides prepared from an edible oil, such as cotton seed oil, have been found to be very satisfactory solubilizing agents.

Examples of saturated mono-hydric alcohols which may be employed as solubilizing agents are 2-ethylhexyl alcohol, n-octyl alcohol, stearyl alcohol, cetyl alcohol and myristyl alcohol.

Examples of the fatty acids which may be employed as solubilizing agents are stearic acid, palmitic acid, oleic acid, lauric acid and myristic acid.

A more comprehensive understanding of this invention is obtained by reference to the following examples:

Example 1.—Sunflower seed oil composition containing mono-stearyl citrate

To 100 grams of refined, winterized, unhydrogenated and deodorized sunflower seed oil is added, 0.10 grams of mono-stearyl citrate. The mixture is preferably heated to approximately 70° C. to effect the uniform dispersion of the mono-stearyl citrate throughout the sunflower seed oil.

The mono-stearyl citrate is prepared as follows:

120 grams of anhydrous citric acid is dissolved in 200 grams of refined, dry pyridine containing 1.8 grams of concentrated sulfuric acid by mechanical agitation while heating on a steam plate at about 95° C. 20 grams of pure stearyl alcohol is then introduced. The stearyl alcohol is quite insoluble in the reaction mixture, a condition favoring mono-ester formation since a small concentration of stearyl alcohol in solution is reacted with a large excess of citric acid. The reaction mixture becomes homogeneous after about 4 hours, after which time the reaction mixture is maintained at 40–50° C. for 16 hours.

The reaction mixture is poured into iced-water containing 75 grams of concentrated sulfuric acid. The aqueous mixture is extracted with ethyl ether, and the ether extract is thoroughly washed with dilute hydrochloric acid and then with water and finally dried with anhydrous sodium sulfate. The ethyl ether solution of mono-stearyl citrate is evaporated, and the residue is crystallized several times from a petroleum ether, the boiling range of which is 80 to 112° C.

A typical melting point of the product is from 74 to 88.5° C., probably depending upon the proportion of symmetrical and unsymmetrical mono-esters present. Other typical characteristics are:

	Found	Calcd.
Acid value	246	253
Saponification value	358	379

Example 2.—Corn oil composition containing mono-stearyl tricarballylate and di-stearyl tricarballylate

10 grams of a mixture of mono-stearyl tricarballylate and di-stearyl tricarballylate is dispersed in 10 kilograms of a corn oil suitable for use as a salad oil or cooking oil. The corn oil prior to the addition of the mixture of the tricarballylic acid esters is heated to a temperature of 35–50° C. The mixture is then agitated to disperse uniformly the mono-stearyl and di-stearyl tricarballylates throughout the oil.

The mono-stearyl tricarballylate and di-stearyl tricarballylate are prepared as follows:

12.1 kilos of tricarballylic acid is added to 30 kilos of commercial stearyl alcohol (containing some palmityl alcohol) which is previously melted. During the addition, the mixture is agitated. The mixture is held at 150° C. under reduced pressure for a period of 1½ hours. At the end of this period, boiling and foaming ceases substantially, corresponding to the completion of the reaction.

Example 3.—Soya bean oil composition containing mono-isopropyl tricarballylate and di-isopropyl tricarballylate

A mixture of mono-isopropyl tricarballylate and di-isopropyl tricarballylate is incorporated in a vegetable oil containing 50% of hydrogenated and deodorized soya bean oil and suitable for the production of margarine. The mono-isopropyl tricarballylate and di-isopropyl tricarballylate are dispersed more effectively throughout the body of the vegetable oil by dissolving the mixture of tricarballylic acid esters in mono-acyl glycerides prepared from the same vegetable oil to which the testers are to be added. The proportions employed are 1 part of the mixture of tricarballylic esters to 4 parts of the mono-acyl glycerides of the vegetable oil. The mono-glycerides may be prepared from the vegetable oil by reacting glycerin with the vegetable oil in the presence of sodium carbonate. The amount of oil and glycerin added is such as to produce predominantly the mono-acyl derivative of the fatty acid components of the oil. Forty grams of the solution of the mixture of tricarballylate esters in the monoglycerides is

added at a temperature of about 35–50° C. to 10 kilograms of the vegetable oil. The composition is then agitated to disperse uniformly the mono-isopropyl tricarballylate and di-isopropyl tricarballylate throughout the oil

The mixture of mono-isopropyl tricarballylate and di-isopropyl tricarballylate is prepared as follows:

260 grams of tricarballylic acid is mixed with 130 grams of commercial isopropyl alcohol, and the mixture is heated at 155° C. for 2 hours in a closed vessel. The pressure developed by the alcohol corresponds to about 55 lbs. per square inch. The alcohol is then evaporated under reduced pressure with a nitrogen stream at 130° C.

Example 4.—Peanut oil composition containing mono-isopropyl isocitrate and di-isopropyl isocitrate

A composition comprising peanut oil is prepared in which there is incorporated mono-isopropyl isocitrate together with di-isopropyl isocitrate and the mono-glycerides of the fatty acid components of substantially any vegetable oil but conveniently the mono-glycerides of the fatty acid components of the peanut oil to which this mixture is added. The mono-isopropyl isocitrate together with the di-isopropyl isocitrate and a negligible quantity of the tri-isopropyl isocitrate and the mono-glycerides are preferably mixed with the oil being treated to form a homogeneous mixture. A solution of the mono-isopropyl isocitrate and di-isopropyl isocitrate in the mono-glycerides of the fatty acid components of peanut oil is prepared by dissolving 1 part of a mixture of the isocitric acid esters in 9 parts of the mono-glycerides. 25 cc. of this solution is added to 10 kilograms of peanut oil. The oil prior to the addition is heated to about 50° C., and during the addition the mixture is agitated.

The mixture of mono-isopropyl isocitrate and di-isopropyl isocitrate is prepared as follows:

Equal parts of isocitric acid and anhydrous isopropyl alcohol are heated together under reflux without catalyst for 118 hours at 92° C. The alcohol and most of the water of reaction are removed by low temperature evaporation in vacuo.

The residue is taken up with ethyl ether and then thrown out of the ether solution by the addition of a quantity of low-boiling petroleum ether just sufficient to form a precipitate. The precipitate or oily residue is again taken up with ethyl ether, and the precipitation with low-boiling petroleum ether repeated. This procedure is repeated several times. The solvent is substantially removed by heating with stirring to 130° C. The product consists of a mixture of about 90% mono-isopropyl isocitrate, about 10% di-isopropyl isocitrate and a negligible amount of tri-isopropyl isocitrate.

Example 5.—Lard composition containing mono-stearyl aconitate and di-stearyl aconitate

3 grams of a mixture of mono-stearyl aconitate and di-stearyl aconitate is heated to a temperature of about 80° C., and these esters are added to 10 kilograms of a lard warmed to liquify it. The composition is agitated to effect dispersion of the mono-stearyl aconitate and the di-stearyl aconitate throughout the liquified lard.

The mixture of mono-stearyl aconitate and di-stearyl aconitate is prepared as follows:

12.1 kilos of aconitic acid are added to 30 kilos of commercial stearyl alcohol which is previously melted. During the addition, the mixture is agitated. The mixture is held at 150° C. under reduced pressure for a period of 1½ hours. At the end of this period, boiling and foaming ceases substantially. The resulting product comprises principally a mixture of mono-stearyl aconitate and di-stearyl aconitate together with a small quantity of tri-stearyl aconitate.

Example 6.—Sunflower seed and cotton seed oil composition containing mono-oleyl tricarballylate and di-oleyl tricarballylate

20 grams of a mixture of mon-oleyl tricarballylate and di-oleyl tricarballylate is added to 10 kilograms of a mixture of equal parts of refined, winterized and deodorized sunflower seed oil and refined, winterized and deodorized cotton seed oil maintained at a temperature of about 50° C. After the esters have been added to the oil mixture, it is thoroughly agitated to effect the uniform dispersion of the esters throughout the oil.

The mixture of mono-oleyl tricarballylate and di-oleyl tricarballylate is prepared as follows:

To 28 kilos of commercial oleyl alcohol is added 10.2 kilos of anhydrous citric acid. During the addition, the mixture is agitated. The mixture is heated and held for a period of about 1¼ hours at 150° C. under reduced pressure. At the end of this period, boiling and foaming ceases substantially. The mixture contains mono-oleyl tricarballylate, di-oleyl tricarballylate and a small quantity of tri-oleyl tricarballylate.

Example 7.—Corn oil composition containing mono-oleyl isocitrate, di-oleyl isocitrate, mono-stearyl isocitrate and di-stearyl isocitrate

5 grams of a mixture containing mono-oleyl isocitrate, di-oleyl isocitrate, mono-stearyl isocitrate and di-stearyl isocitrate together with a small quantity of tri-oleyl isocitrate, tri-stearyl isocitrate and mixed isocitric acid esters of oleyl and stearyl alcohols are melted and added to 10 kilograms of corn oil heated to about 50° C. During the addition, the mixture is agitated to effect a uniform dispersion of the mono- and di-esters of isocitric acid throughout the body of the oil.

The mixture of mono-oleyl isocitrate, di-oleyl isocitrate, mono-stearyl isocitrate and di-stearyl isocitrate is prepared as follows:

A mixture of 14 kilograms of commercial oleyl alcohol and 14 kilograms of commercial stearyl alcohol is melted, and to this mixture is added 10.2 kilograms of isocitric acid. During the addition, the mixture is agitated. The mixture is heated and held for a period of 1¼ hours at 150° C. while passing nitrogen through at atmospheric pressure. At the end of this period, boiling and foaming ceases substantially. The mixture contains mono-oleyl isocitrate, di-oleyl isocitrate, mono-stearyl isocitrate, di-stearyl isocitrate together with a small quantity of tri-stearyl isocitrate and tri-oleyl isocitrate and the mixed isocitric acid esters of oleyl and stearyl alcohols.

Example 8.—Soya bean and sunflower seed oil composition containing lauryl isocitrate

8 grams of a mixture of mono-laury isocitrate and di-lauryl isocitrate is added to 1 kilogram of hydrogenated margarine oil (Wiley M. P. 94° F.) consisting of a mixture of equal parts of hydrogenated and deodorized soya bean oil and hydrogenated and deodorized sunflower seed oil maintained at a temperature of 50° C. After the esters have been added to the oil mixture, it is thoroughly agitated to effect uniform dispersion of the composition throughout the oil.

The mixture of mono-lauryl isocitrate and di-lauryl isocitrate is prepared as follows:

120 grams of isocitric acid is added to 250 grams of commercial lauryl alcohol. During the addition, the mixture is agitated. The mixture is held at 150° C. under reduced pressure (about 25–100 mm.) for a period of 1½ hours. At the end of this period, boiling and foaming ceases substantially. The resulting product comprises principally a mixture of mono-lauryl isocitrate and di-lauryl isocitrate together with a small quantity of tri-lauryl isocitrate.

Example 9.—Soya bean and peanut oil composition containing mono-stearyl aconitate and di-stearyl aconitate

A mixture of mono-stearyl aconitate and di-stearyl aconitate is incorporated in a margarine oil containing 75% of hydrogenated and deodorized soya bean oil and 25% of hydrogenated and deodorized peanut oil. The mono-stearyl aconitate and di-stearyl aconitate are dispersed more effectively throughout the body of the vegetable oil by dissolving the mixture of the aconitic acid esters prepared from the same mixture of vegetable oils to which the esters are to be added. The proportions employed are 1 part of the mixture of aconitic acid esters to 4 parts of mono-acyl glycerides of the vegetable oil. The mixture of mono-stearyl aconitate and di-stearyl aconitate for this purpose is prepared in the manner described in Example 5.

20 grams of the solution of the mixture of aconitic acid esters in the mono-glycerides is added at a temperature of 35–50° C. to 1 kilogram of the mixture of hydrogenated and deodorized soya bean and peanut oils. The composition is then agitated to disperse uniformly the mono-stearyl aconitate and di-stearyl aconitate throughout the oil.

Example 10.—Cottonseed and sunflower seed oil composition containing mono-oleyl tricarballylate and di-oleyl tricarballylate

9 grams of a mixture of mono-oleyl tricarballylate and di-oleyl tricarballylate is added to 1 kilogram of a mixture of 75% of hydrogenated and deodorized cottonseed oil and 25% of hydrogenated and deodorized peanut oil maintained at a temperature of about 50° C. After the addition of the esters to the oil mixture, the mixture is thoroughly agitated to effect the uniform dispersion of the esters throughout the oil. The mixture of mono-oleyl tricarballylate and di-oleyl tricarballylate is prepared in the same manner as the mixture of these esters are produced in accordance with the method described in Example 6.

The oil composition described in Examples 3, 8, 9, and 10 are particularly useful as the oil component of margarine.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of an unsymmetrical hydroxy aliphatic poly-carboxylic acid containing at least 3 carboxyl groups and which contains no functional groupings other than the hydroxyl and carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

2. A food composition comprising a significant amount of a glyceridic oil having incorporated 0.002 to 0.1% by weight on said oil of a mono-alkylene ester of a simple functional aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

3. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of an unsymmetrical hydroxy aliphatic poly-carboxylic acid containing at least 3 carboxyl groups and which contains no functional groupings other than hydroxyl and carboxyl groups, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

4. A food composition comprising a significant amount of a glyceridic oil having incorporated 0.002 to 0.1% by weight on said oil of a mono-alkylene ester of a simple functional aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

5. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.06 to 1.9% by weight on said oil of a di-alkyl ester of a simple functional sunsaturated aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

6. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.06 to 1.9% by weight on said oil of a di-alkyl ester of a simple functional unsaturated aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

7. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of an unsymmetrical hydroxy aliphatic tri-carboxylic acid which contains no functional groupings other than hydroxyl and carboxyl groups, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

8. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkylene ester of a simple functional aliphatic tri-carboxylic acid, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

9. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.06 to 1.9% by weight on said oil of a di-alkyl ester of an unsaturated simple functional aliphatic tri-carboxylic acid, the primary ionization constant of said acid being within the range 1.7×10^{-3} and 1.0×10^{-4} at 25° C.

10. A food composition comprising a significant amount of a glyceridic oil having incorporated therein an amount of an ester selected from the class consisting of 0.002 to 0.1% by weight on said oil of mono-alkyl and mono-

alkylene esters of a poly-carboxylic acid and 0.06 to 1.9% by weight on said oil of di-alkyl and di-alkylene esters of a poly-carboxylic acid, said poly-carboxylic acid being selected from the class consisting of simple functional aliphatic poly-carboxylic acids containing at least 3 carboxyl groups and unsymmetrical hydroxy aliphatic poly-carboxylic acids containing at least 3 carboxyl groups and having no functional groupings other than the hydroxyl and carboxyl groups, the primary ionization constant of said acids being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

11. The method of producing an improved food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said glyceridic oil an amount of an ester selected from the class consisting of 0.002 to 0.1% by weight on said oil of mono-alkyl and mono-alkylene esters of a poly-carboxylic acid and 0.06 to 1.9% by weight on said oil of di-alkyl and di-alkylene ester of a poly-carboxylic acid, said poly-carboxylic acid being selected from the class consisting of simple functional aliphatic poly-carboxylic acids containing at least 3 carboxyl groups and unsymmetrical hydroxy aliphatic poly-carboxylic acids containing at least 3 carboxyl groups and having no functional groupings other than the hydroxyl and carboxyl groups, the primary ionization constant of said acids being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

12. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of aconitic acid.

13. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of isocitric acid.

14. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.06 to 1.9% by weight on said oil of a di-alkyl ester of aconitic acid.

15. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of a mono-alkylene ester of tricarballylic acid.

16. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of mono-isopropyl isocitrate.

17. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.06 to 1.9% by weight on said oil of di-stearyl aconitate.

18. A food composition comprising a significant amount of a glyceridic oil having incorporated therein 0.002 to 0.1% by weight on said oil of mono-oleyl tricarballylate.

19. The method of producing an improved food composition comprising a significant amount of a glyceridic oil, said method comprising incorporation in said glyceridic oil 0.002 to 0.1% by weight on said oil of a mono-alkyl ester of an unsymmetrical hydroxy aliphatic poly-carboxylic acid containing at least 3 carboxyl groups and which contains no functional groupings other than the hydroxyl and carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

20. The method of producing an improved food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said glyceridic oil 0.002 to 0.1% by weight on said oil of a mono-alkylene ester of a simple functional aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

21. The method of producing an improved food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said glyceridic oil 0.06 to 1.9% by weight on said oil of a di-alkyl ester of a simple functional unsaturated aliphatic poly-carboxylic acid containing at least 3 carboxyl groups, the primary ionization constant of said acid being within the range 1.0×10^{-2} and 1.0×10^{-4} at 25° C.

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