

# UNITED STATES PATENT OFFICE

2,485,632

## GLYCERIDIC OIL COMPOSITION AND METHOD OF PREPARING SAME

Hans W. Vahlteich, Edgewater, and Ralph H. Neal, Jersey City, N. J., and Chester M. Gooding, Staten Island, N. Y., assignors to The Best Foods, Inc., New York, N. Y., a corporation of New Jersey

No Drawing. Application July 31, 1945,  
Serial No. 608,102

14 Claims. (Cl. 99—163)

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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 retard for relatively prolonged periods the development of rancidity of 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.

Another object of this invention is to retard the development of off-flavor or flavor reversion in glyceridic oils.

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 certain glyceridic oils, there sometimes develops an off-flavor which is ordinarily called flavor reversion. This development of off-flavor appears to be different from the rancidity of the oil and is usually discernible before the rancidity becomes manifest quantitatively.

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 long period. These compositions comprise a glyceridic oil or a plurality of glyceridic oils and a monoester of citric acid, for example a monoaliphatic ester of citric acid, such as a monoalkyl or a monoalkylene ester of citric acid. With some glyceridic oils, the addition of the monoaliphatic ester of citric acid prevents the development of the off flavor due to the spontaneous hydrolysis of glycerides to free fatty acids. In some cases, the monoester of citric acid is not soluble or miscible to a sufficient degree in the glyceridic oil to produce a substantially homogeneous composition. To disperse the monoester of citric acid throughout the glyceridic oil, an oil-soluble hydrophilic coupling agent is employed. Examples of satis-

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factory oil-soluble hydrophilic coupling agents for this purpose are the diesters and triesters of citric acid, oil-soluble aliphatic alcohols having at least 6 carbon atoms, monocarboxylic acids having at least 10 carbon atoms and monoglycerides of monocarboxylic acids in which the acyl group has at least 10 carbon atoms. When an oil-soluble hydrophilic coupling agent is employed, the monoester of citric acid is first dissolved in the oil-soluble hydrophilic coupling agent, and the resulting mixture is incorporated in the glyceridic oil. The diesters and triesters of citric acid have been found very satisfactory for solubilizing the monoester of citric acid. The incorporation in glyceridic oil, and particularly in refined, hydrogenated and deodorized glyceridic oil, of a mixture of monoesters and diesters of citric acid or a mixture of monoesters, diesters and triesters of citric acid, has been found effective for preventing the development of the off-flavor.

The compositions of this invention may be substantially all oil systems, such as shortening, or aqueous and oil systems, such as margarine. In the aqueous and oil system, the nicety of balance between the hydrophilic components and lipophilic components may be achieved by regulating the proportions of the monoester of citric acid and the hydrophilic coupling agent added to the glyceridic oil. In the all oil system, by adding a sufficient quantity such as 0.1 to 10% of certain monoesters of citric acid 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 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 low ratio shortening. Certain monoesters of citric acid alone or in combination with a hydrophilic coupling agent such as a monoglyceride of a monocarboxylic acid or a mixture of di- and triesters of citric acid or both have been found to have marked emulsifying characteristics.

The ability of the compositions of this invention to retard rancidity is best demonstrated by an examination of the results of the comparative testing under identical conditions of corn salad oil containing monostearyl citrate, the same corn salad oil containing distearyl citrate, and the



same corn salad oil to which no ester of citric acid was added. All samples of oils were maintained at 95° F. for 62 days and the peroxide value of the oils determined periodically. The results of this testing were as follows:

Peroxide values (millimols)

Days.....	4	7	9	14	20	23	29	37	43	49	62
Control (Corn Salad Oil).....	1.3	1.9	3.0	5.3	8.0	10.2	15.1	21.8	30.5	36.3	52.6
Control+0.0125% Monostearyl-citrate.....	1.0	0.9	1.2	1.9	2.6	3.3	5.6	9.0	13.5	17.9	33.0
Control+0.02% Distearyl citrate.....	1.7	2.5	3.7	6.4	9.7	12.0	17.2	19.9	31.5	37.3	56.2
Control+0.10% Monostearyl citrate.....	1.0	1.0	1.2	2.0	2.5	3.2	5.2	7.1	11.2	14.9	26.4
Control+0.16% Distearyl citrate.....	1.8	2.7	4.0	6.9	10.4	12.4	17.0	20.9	28.9	34.7	49.1

It is observed that, while the peroxide values of the corn salad oil containing the distearyl citrate were substantially the same as those of the control, the development of rancidity in the corn salad oil to which monostearyl citrate was added was materially reduced.

Another comparative test of the compositions of this invention with compositions of the same oil to which the corresponding diester of citric acid was added and the oil to which no ester of citric acid was added again shows the efficacy of the compositions of this invention in retarding the development of rancidity in oils. In this testing a sample of cottonseed oil to which monostearyl citrate was added was tested under identical conditions with the same cottonseed oil to which distearyl citrate was added, and another sample of the same cottonseed oil to which no ester was added.

These samples were subjected simultaneously to aeration at a temperature of about 100° C. for a period of hours until the rancid point was reached, in accordance with the method described in Oil and Soap (volume 10, #6, pages 105 to 109, June 1933). The iodine number (Wijs) of the deodorized cottonseed oil employed in this test was about 71.5.

The results obtained by this testing are given in the following table:

Composition	Hrs. to End Point (Peroxide Number 100)
Control—Deodorized Cottonseed Oil without any Addition.....	31
Deodorized Cottonseed Oil+0.025% Monostearyl Citrate.....	32
Deodorized Cottonseed Oil+0.04% Distearyl Citrate.....	70
	69
	38
	42

Here again, while the distearyl citrate increased by a small amount the active oxygen test value, the addition of the monostearyl citrate increased the value more than two fold.

The advantage from a flavor standpoint in the case of some of the glyceridic oil compositions of this invention is shown by a comparison of the flavor of potato chips produced by frying in lard to which monostearyl citrate was added, the same lard to which distearyl citrate was added, and the same lard to which no ester of citric acid was added. These potato chips, after preparation under identical conditions, were stored for a period of five weeks and their flavor determined by a number of experts skilled in discerning flavor differences. Moreover, in order to determine the amount of rancidity of the oil in the potato chips after this five week period, the oil in the potato chips was extracted and the peroxide value of that oil ascertained.

In the production of the potato chips, raw

slices of potatoes were immersed in the heated lard initially at a temperature of about 355° F. Upon introduction of the potato chips, the temperature dropped appreciably and the oil was heated further until a temperature of about

320° F. was attained. At this point the potato chips developed a dark brown color and were considered suitably fried. This is a common procedure for preparing potato chips. The potato chips were then withdrawn and permitted to drain to remove the surplus fat. The potato chips so prepared were then stored at room temperature for a period of five weeks. The flavor as ascertained by a scoring panel of four experts was as follows:

Lard	Compound Added	Flavor of Potato Chips After 5 Weeks at Room Temp.
Neutral.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	Poor—rancid. Fair—strong. Poor—rancid.
Proprietary Brand A.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	Poor—rancid. Fairly good—lardy (not rancid). Poor—rancid.
Brand B.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	Poor—rancid. Fairly good—lardy (not rancid). Poor—rancid.
Commercial Bulk.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	Poor—rancid. Fairly good—lardy (not rancid). Poor—rancid.

It is observed that with all of the lards tested, a definite improvement was obtained by the addition of the monostearyl citrate over the sample of lard to which no monostearyl citrate was added, and also that the lard to which distearyl citrate was added approached the flavor of the control sample to which no ester was added.

After the five week period, the oil in the potato chips was extracted and tested for peroxide number. The results of this testing are given in the following table:

Lard	Compound Added	Peroxide No. of Fat Extracted After 5 Weeks Storage at Room Temp.
Neutral.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	294 220 227
Brand A.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	58 49 325
Brand B.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	376 113 359
Commercial Bulk.....	{None—Control..... 0.05% monostearyl citrate..... 0.05% distearyl citrate.....	277 15 211

While with the neutral and brand A lard, only appreciable advantage could be observed in the samples to which the monostearyl citrate was added, in brand B and the commercial bulk lard a definite improvement was observed.

It would appear that the addition of mono-



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esters of citric acid to lard is effective in retarding the flavor deterioration of potato chips cooked in lard containing the monoester of citric acid. Although with some glyceridic oils a flavor improvement is not discernible, with a great number the addition of the monoesters of citric acid to the oil results in a marked improvement in their flavor characteristics.

Although the values given in the data outlined in the above tables are believed to be typical and representative of glyceridic oils, variations will appear among such oils, particularly among different glyceridic oils. In some of these oils the improvement by the addition of the monoester is more marked than in others. However, all glyceridic oils are improved to at least some degree.

Some of the monoesters of citric acid are soluble only to a limited degree in glyceridic oils or mixtures containing glyceridic oils. This is particularly true of the monoalkyl esters of citric acid in which the alkyl group has less than 10 carbon atoms. While the oil may be heated to dissolve some of these monoesters, such heating, particularly if a high temperature is required, materially damages the oil for some purposes. To facilitate the uniform dispersion of the monoesters throughout the body of the oil, an oil-soluble coupling agent is employed. The monoester is dissolved in the coupling agent and the resulting solution mixed, desirably with agitation, throughout the body of the oil. Among the coupling agents that are satisfactory for this purpose are monoacyl glycerides, preferably monoacyl glycerides in which the acyl radical has at least 10 carbon atoms, saturated monohydric alcohols, preferably saturated monohydric alcohols having at least 6 carbon atoms, fatty acids having at least 10 carbon atoms, diesters of citric acid such as dialiphatic esters of citric acid, for example, dialkyl citrates in which the alkyl group has at least 10 carbon atoms and triesters of citric acid such as trialiphatic esters of citric acid, for example, trialkyl citrate in which the alkyl group has at least 10 carbon atoms.

Examples of monoacyl glycerides which may be employed as coupling agents are the mono-*stearyl* glycerides, mono-*oleyl* glycerides, mono-*lauryl* glycerides and mono-*palmityl* glycerides or mixtures thereof. These monoacyl glycerides as commercially prepared contain substantial amounts of the corresponding diacyl glycerides and traces of the corresponding triacyl glycerides; such monoacyl glycerides as commercially prepared may be employed as the coupling agents in the compositions of this invention.

Examples of saturated monohydric alcohols which may be employed as coupling 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.

Examples of the monoesters which may be employed in the compositions of this invention are *ethyl* citrate, *n*-*propyl* citrate, *isopropyl* citrate, *n*-*butyl* citrate, *crotyl* citrate, *isobutyl* citrate, *isoamyl* citrate, 2-ethylhexyl citrate, *lauryl* citrate, *myristyl* citrate, *palmityl* citrate, *oleyl* citrate and *stearyl* citrate.

Examples of the dialiphatic esters of citric acid such as dialkyl esters of citric acid and dialkylene esters of citric acid which may be employed as solubilizing or coupling agents for the monoali-

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phatic esters of citric acid are the dialiphatic citric acid esters corresponding to the monoaliphatic citric acid esters heretofore listed. Likewise, examples of the trialiphatic esters of citric acid which may be employed as coupling agents are those corresponding to the monoaliphatic esters of citric acid heretofore specifically noted.

Mixtures of the monoaliphatic esters of citric acid may be employed in the compositions of this invention. For example, a mixture of different monoalkyl esters of citric acid may be added to the glyceridic oil, or again, different monoalkylene monoesters of citric acid may be added to the glyceridic oil; or a mixture of a monoalkyl ester and a monoalkylene ester may be employed. Likewise, mixtures of dialiphatic esters of citric acid or trialiphatic esters of citric acid may be utilized as solubilizing agents. In fact, it has been found convenient to produce the solubilizing agent simultaneously with the monoaliphatic esters of citric acid. This end can be conveniently achieved by reacting an appropriate amount of citric acid with an aliphatic alcohol such as an alkyl or alkylene alcohol to produce the required amount of the monoaliphatic esters of citric acid together with sufficient amounts of the corresponding di- and/or triesters of citric acid to effect solubilizing of the monoesters in the glyceridic oil.

Again mixtures of various solubilizing agents may be utilized to effect uniform dispersion of the monoaliphatic esters of citric acid throughout the glyceridic oil. For example, a mixture of *lauryl* alcohol, *cetyl* alcohol, *distearyl* citrate and *tristearyl* citrate may be employed to effect the solubilizing of mono-*isopropyl* citrate in the glyceridic oil. Alternately, a mixture of different monoacyl glycerides may be utilized for the solubilizing of the monoesters.

The monoesters used in the composition of this invention are new compounds and are prepared by the esterification of citric acid and a monohydric alcohol preferably in proportions which favor the formation of the monoesters. The esterification may be conducted by any of the well known methods employed for the production of esters, and the resulting reaction mixture which comprises not only the monoesters of citric acid but small amounts of di- and triesters of citric acid is subjected to treatment with solvents which dissolve the monoesters but do not dissolve any appreciable amounts of the di- and triesters, or alternately solvents which dissolve the di- and triesters but do not dissolve appreciable quantities of the monoesters. By repeating the treatment with these solvents, a relatively pure monoester of citric acid may be obtained. For example, a monohydric primary alkyl alcohol may be reacted with anhydrous citric acid dissolved in a solvent such as dry pyridine. The amounts of citric acid and alcohol employed are desirably those which favor the formation of the monoester. For this purpose, an amount of citric acid in excess of that required to react with the alcohol to produce the monoester is employed. The reaction mixture is heated for a period of from 4 to 6 hours at about 100° C., after which the reaction mixture is maintained for a period of from 14 to 20 hours at about 40 to 50° C. The resulting reaction product is then poured into a water-ice mixture containing a sufficient quantity of concentrated sulfuric acid to react with the pyridine in the mixture to form pyridine sulfate. A solvent such as a low boiling petroleum ether in which the di- and triesters are relatively soluble, but in which the monoester is relatively insol-



uble, is employed to effect a separation of the monoester from the small amounts of the di- and triesters in the reaction mixture. The aqueous mixture is extracted first with ethyl ether in which the monoester as well as the di- and triester is relatively soluble. To this ethyl ether extract is added a relatively large quantity of low boiling petroleum ether in which the monoester is substantially insoluble, but in which the di- and triesters are relatively soluble. This precipitates the monoester. If further purification is desired, this precipitate or oily residue is again dissolved in ethyl ether, and the procedure repeated. Some of the di- and triesters employed as coupling agents are also new, and these di- and triesters are produced by reacting citric acid and the required alcohol in amounts which favor the formation of either the di- or triester. The di- and triesters may be separated from each other and from any monoester contained therein by fractional crystallization with a suitable solvent such as ethyl alcohol.

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

*Example 1.—Sunflower oil composition containing monostearyl citrate*

To 100 grams of refined, winterized, unhydrogenated but deodorized sunflower oil is added 0.10 gram of monostearyl citrate. The mixture is preferably heated to approximately 80° C. to effect the relatively uniform dispersion of the monostearyl citrate throughout the sunflower oil.

The monostearyl citrate is a new compound and is prepared as follows:

120 grams of anhydrous citric acid are 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 are then introduced. The stearyl alcohol is quite insoluble in the reaction mixture, a condition favoring monoester 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 monostearyl 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 monoesters present. Other typical characteristics are:

	Found	Cal'd
Acid Value.....	246	253
Saponification Value.....	358	379

*Example 2.—Corn oil composition containing monoisopropyl citrate*

One gram of monoisopropyl citrate is dissolved in 5 grams of monoacyl glycerides prepared from a winterized, refined unhydrogenated but deodorized corn oil. The monoglycerides are prepared

from this corn oil by reacting glycerine with the corn oil in the presence of sodium bicarbonate. The amount of oil and glycerine added are such as to produce predominantly the monoacyl derivatives of the fatty acid components of the corn oil. The solution of the monoisopropyl citrate is added at a temperature of about 35 to 50° C. to 10 kilograms of a winterized refined, unhydrogenated, but deodorized corn oil suitable for use as a cooking and salad oil. The corn oil prior to the addition of the solution of the monoisopropyl citrate is heated to a temperature of 35 to 50° C. The mixture is then agitated to disperse uniformly the monoisopropyl citrate throughout the oil.

The monoisopropyl citrate is a new compound and is prepared as follows:

Equal parts of USP citric acid and anhydrous isopropyl alcohol are heated together under reflux, without catalyst for 118 hours at 92° C., after which time the acid value of the reaction mixture is found to be about 203.6 and the saponification value 392 (one-half esterified). 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. After final removal of solvent by heating with stirring to 130° C. a typical analysis is:

	Found	Calc'd
Acid Value.....	454	480
Saponification Value.....	709	720

This product solidifies after long standing and consists of a mixture of about 90% monoester and 10% diester. The resulting product, without further purification, may be used in the corn oil composition heretofore described or any other glyceridic oil composition.

*Example 3.—Peanut oil composition containing monostearyl citrate*

A composition of hydrogenated and deodorized peanut oil having an iodine value of about 60 and monostearyl citrate is conveniently prepared by first producing a mixture of the monostearyl citrate, distearyl citrate and tristearyl citrate and adding the resulting mixture to the peanut oil. In this way, the distearyl citrate and tristearyl citrate act as solubilizing agents for the monostearyl citrate, and the monostearyl citrate retards markedly the development of rancidity of the peanut oil. The mixture of monostearyl citrate, distearyl citrate and tristearyl citrate for this purpose is prepared as follows:

12.1 kilograms of citric acid monohydrate are added to 30 kilograms 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 which consists of a mixture of monostearyl citrate, distearyl citrate and tristearyl citrate has an acid value of about 83, a saponification value of about 249.0 and a melting



point of about 51–68° C. and a color on the Lovibond scale of about 36Y–5.8R (5¼ inch column).

Five grams of the mixture of monostearyl citrate, distearyl citrate and tristearyl citrate heated to about 65° C. are added to 10 kilograms of hydrogenated and deodorized peanut oil maintained at a temperature of about 60° C. During the addition the mixture is agitated.

**Example 4.—Soya bean oil composition containing monooleyl citrate and monostearyl citrate**

A mixture of monooleyl citrate and monostearyl citrate are employed for retarding the rancidity of a vegetable oil containing 50% soya bean oil and suitable for the production of margarin. To disperse better the monostearyl citrate and the monooleyl citrate throughout the body of the vegetable oil containing hydrogenated and deodorized soya bean oil, the monostearyl citrate and the monooleyl citrate are prepared in such a manner as to produce simultaneously their corresponding di- and triesters together with mixed esters of oleyl alcohol and stearyl alcohol. A mixture of mono-, di- and tricitric acid esters derived from stearyl alcohol and oleyl alcohol is prepared by employing proportions of citric acid and oleyl and stearyl alcohol to produce a ratio of mono-, di- and triesters to effect the solubilizing of the monoesters.

A mixture of monostearyl citrate, monooleyl citrate and their corresponding di- and triesters together with the mixed esters 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 are added 10.2 kilograms of anhydrous citric acid. During the addition the mixture is agitated. The mixture is heated and held for a period of 1¼ hours at 150° C. under reduced pressure. At the end of this period boiling and foaming ceases substantially. The mixture contains monostearyl citrate, monooleyl citrate and their corresponding di- and triesters together with the mixed citric acid esters of oleyl and stearyl alcohols. 2.5 grams of this mixture containing monostearyl citrate, monooleyl citrate and their corresponding di- and triesters together with the mixed esters are melted and added to 10 kilograms of a vegetable oil containing about 50% of hydrogenated and deodorized soya bean oil and the remainder hydrogenated and deodorized peanut oil heated to about 50° C. During the addition the mixture is agitated to effect a uniform dispersion of the monoesters throughout the oil.

**Example 5.—Corn oil composition containing monoisopropyl citrate**

A composition comprising corn salad oil in which is incorporated the monoisopropyl citrate together with the diisopropyl citrate and triisopropyl citrate and the monoglycerides of the fatty acid components of substantially any vegetable oil, but conveniently the monoglycerides of the fatty acid components of the corn salad oil to which this mixture is added. The monoisopropyl citrate together with its solubilizing agents consisting of the diisopropyl citrate and triisopropyl citrate and the monoglycerides are preferably mixed with a quantity of the oil being treated to form a homogeneous mixture. As in Examples 3 and 4, since the diisopropyl citrate and triisopropyl citrate are employed as solubilizing agents, these compositions are prepared

simultaneously with the monoisopropyl citrate. The mixture of esters is produced as follows:

260 grams of anhydrous citric acid are 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. A typical acid value of the resulting product is 386 and a typical saponification value 702. A typical ratio of free carboxyl to total carboxyl is 0.55.

38 parts of these mixed isopropyl esters of citric acid are dissolved in 44.3 parts of monoglycerides prepared as described in Example 2 together with 17.7 parts of the corn salad oil to be treated. Preferably the 17.7 parts of the oil to be treated are added to the crude monoglycerides after their preparation and before washing. This procedure aids in separation of the wash water and decreases the degree of spontaneous esterification of the free carboxyl groups of the isopropyl citrates by the free hydroxyl groups of the monoglycerides. The washing with water, moreover, removes excess glycerin.

10 cc. of the solution of the monoglycerides containing the mixed isopropyl esters are added to 10 kilograms of corn salad oil. The oil prior to the addition is heated to a temperature of about 50° C., and during the addition the mixture is agitated.

**Example 6.—Sunflower seed and cottonseed oil composition containing monostearyl citrate**

One kilogram of monostearyl citrate, one kilogram of distearyl citrate and two kilograms of tristearyl citrate are heated to a temperature of about 80° C., and these esters are added to 7,000 kilograms of a mixture of equal parts of refined, winterized, and deodorized sunflower seed oil and refined, winterized, and deodorized cottonseed oil heated to a temperature of about 55° C. The composition is agitated to effect dispersion of the monostearyl citrate throughout the oil. The distearyl citrate and tristearyl citrate are employed as solubilizing agents and are prepared as follows:

These esters are obtained by fractional crystallization of the mixed stearyl citrate esters described in Example 3. By use of 750 cc. of ethyl alcohol, from 150 grams of mixed esters, there are obtained about 21.8 grams of triesters from the first three fractions. In a typical run, the 4th, 5th and 6th fractions yield a total of about 49.4 grams of fairly pure diesters. The combined diesters are recrystallized from anhydrous isopropyl alcohol and finally from acetone. The melting point range is about 69°–72° C. When supercooled (to 50° C.) double melting points are observed at about 53° C. with resolidification and a second melting point of 72° C. The following is a typical analysis:

	Found	Calc'd
Acid Value.....	76.4	80.6
Saponification Value.....	240.2	241.8

**Example 7.—Sunflower seed oil composition containing monoisopropyl citrate**

5 parts of mixed isopropyl citrate prepared in accordance with the procedure outlined in Example 5 are dissolved in 20 parts of oleyl alcohol.



25 cc. of this solution are added to 5 kilos of unhydrogenated and undeodorized sunflower seed oil. During the addition of the solution of the mixed isopropyl citrates, the mixture is agitated vigorously.

*Example 8.—Lard composition containing monoisopropyl citrate*

Monoisopropyl citrate may be added to lard and dispersed uniformly therethrough by the use of the corresponding di- and triesters and stearic acid. A mixture for this purpose may be conveniently prepared as follows:

25 parts of mixed isopropyl esters of citric acid prepared as described in Example 5 are heated with 125 parts of commercial stearic acid to about 120° C., with vigorous stirring in an inert atmosphere for ½ hour. The mixture is substantially homogeneous soon after passing 100° C. and remains so down to the solidification temperature of the stearic acid used as one of the coupling agents.

6 cc. of the solution of the mixed isopropyl esters and stearic acid as heretofore described are added to 10 kilograms of commercial bulk lard heated to about 50° C. During the addition, the lard is agitated vigorously.

*Example 9.—Lard composition containing monoethyl citrate*

Monoethyl citrate is added to commercial lard. The monoethyl citrate is rendered soluble in the lard composition by diethyl citrate, triethyl citrate and monoglycerides of the fatty acid components of the oil to which it is added. The monoethyl citrate is preferably prepared simultaneously with the diethyl citrate and triethyl citrate by the method hereinafter described, and the mixture of mono-, di- and triethyl citrates is dissolved in the monoglycerides prepared from the lard. 50 grams of the mixture of mono-, di- and triethyl citrates are added to 50 grams of the monoglycerides. The monoglycerides are prepared in the same manner as the mono-glycerides in Example 2. The amount of monoethyl citrate in the mixture of mono-, di- and triethyl citrates is about 75%. 1 cc. of the solution of the mixture of ethyl citrates in the monoglycerides is added to 1 kilogram of lard maintained at a temperature of about 50° C. and agitated to effect dispersion of the composition throughout the oil.

The mixture of monoethyl citrate, diethyl citrate and triethyl citrate is prepared as follows: 96 grams of anhydrous citric acid and 300 cc. of absolute ethanol are refluxed for 3 days. The excess ethanol is removed by evaporation on a steam bath. Analysis of the resulting mixture shows the following acid and saponification values:

Acid value	258.2
Saponification value	680.7

What is claimed is:

1. A food product comprising a significant amount of a glyceridic oil having incorporated therein a monoester of citric acid, the amount of said monoester being not more than 0.1% of said glyceridic oil by weight.

2. A food product comprising a significant amount of a glyceridic oil having incorporated therein a monoalkyl ester of citric acid, the amount of said monoalkyl ester being not more than 0.1% of said glyceridic oil by weight.

3. A food product comprising a significant

amount of a glyceridic oil having incorporated therein a monoalkylene ester of citric acid, the amount of said monoalkylene ester being not more than 0.1% of said glyceridic oil by weight.

4. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monoalkyl ester of citric acid, the amount of said monoalkyl ester being not more than 0.1% of said glyceridic oil by weight.

5. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monoalkylene ester of citric acid, the amount of said monoalkylene ester being not more than 0.1% of said glyceridic oil by weight.

6. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monoalkyl ester of citric acid and a mutual solvent for said monoalkyl ester and said oil, the amount of said monoalkyl ester being not more than 0.1% of said glyceridic oil by weight.

7. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monoalkylene ester of citric acid and a mutual solvent for said monoalkylene ester and said oil, the amount of said monoalkylene ester being not more than 0.1% of said glyceridic oil by weight.

8. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monoalkyl ester of citric acid and a monoglyceride of a monocarboxylic acid in which the acyl group has at least 10 carbon atoms, the amount of said monoalkyl ester being not more than 0.1% of said glyceridic oil by weight.

9. A food product comprising a significant amount of a hydrogenated and deodorized glyceridic oil having incorporated therein a monostearyl citrate, the amount of said monostearyl citrate being not more than 0.1% of said glyceridic oil by weight.

10. A method of retarding the development of rancidity of a food product comprising a significant amount of a glyceridic oil, said method comprising incorporated in said oil a monoaliphatic ester of citric acid, the amount of said monoaliphatic ester incorporated in said oil being not more than 0.1% of said glyceridic oil by weight.

11. A method of retarding the development of rancidity of a food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said oil a monoalkyl ester of citric acid, the amount of said monoalkyl ester incorporated in said oil being not more than 0.1% of said glyceridic oil by weight.

12. A method of retarding the development of rancidity of a food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said oil a monoalkylene ester of citric acid, the amount of said monoalkylene ester incorporated in said oil being not more than 0.1% of said glyceridic oil by weight.

13. A method of retarding the development of rancidity of a food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said oil a monoalkyl ester of citric acid dissolved in a mutual solvent for said monoalkyl ester and said oil, the amount of said monoalkyl ester incorporated in said oil being not more than 0.1% of said glyceridic oil by weight.

14. A method of retarding the development of



rancidity of a food product comprising a significant amount of a glyceridic oil, said method comprising incorporating in said oil a monoalkylene ester of citric acid dissolved in a mutual solvent for said monoalkylene ester and said oil, the amount of said monoalkylene ester incorporated in said oil being not more than 0.1% of said glyceridic oil by weight.

HANS. W. VAHLTEICH.  
RALPH H. NEAL.  
CHESTER M. GOODING.

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