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COMPOSITIONS, INCLUDING ESTERS OF CITRIC ACID

Hans W. Vahlteich, Edgewater, and Ralph H. Neal, North Bergen, 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

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This is a continuation-in-part application of the applications Serial Numbers 608,101, now Pat-No. 2,485,631, and 608,102, now Pat. 2,485,632, filed July 31, 1945, and the application Serial Number 608,380, now Pat. 2,485,633, filed August 1, 1945.

This invention relates to citric acid ester compositions, and more particularly to compositions including esters of citric acid.

An object of this invention is to disperse relatively readily and uniformly esters of citric acid, and particularly monoesters or diesters of citric acid throughout a mass of oil.

Another object of this invention is to provide compositions which retard the development of rancidity and off-flavor in glyceridic oils and which may be quickly disseminated throughout a mass of glyceridic oil.

Another object of this invention is to incorporate in glyceridic oils monoesters or diesters of citric acid which due to their limited solubility or relative immiscibility per se in glyceridic oils, are difficult to incorporate therein.

Monoesters of citric acid have been found to retard for relatively prolonged periods rancidity in glyceridic oils, while mixtures of mono, di and triesters of citric acid are effective as emulsifiers. Some of these esters of citric acid, however, particularly the lower mono and di-alkyl esters of citric acid, due to their limited solubility or relative immiscibility in the oil, are not readily dispersed uniformly throughout a mass of oil. And to retard effectively the development of rancidity and off-flavor of these oils, it is essential that the esters of citric acid be dispersed relatively uniformly throughout the mass of the oil.

In accordance with this invention, compositions comprising esters of citric acid are provided which may be readily dispersed throughout a mass of oil. These compositions comprise a solubilizing agent and an ester of citric acid, such as a mono or di-alkyl ester of citric acid or a mono or dialkylene ester of citric acid. These compositions may contain a plurality of citric acid esters, such as a mixture of mono, di and triesters of citric acid which may be derived from the same or a plurality of different alcohols and citric acid. The solubilizing agent may be, for example, a monocarboxylic acid having at least 10 carbon atoms; a monocarboxylic acid monoester of glycerol or propylene glycol or their polymers, the monocarboxylic acid having at least 10 carbon atoms; a phosphatide such as lecithin; an oil-soluble aliphatic alcohol having at least 6 carbon atoms, esters of polyhydric alcohols or

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their polymers; or ethers and anhydrides of polyhydric alcohols.

The compositions of this invention may be readily dispersed uniformly throughout a mass of oil, such as glyceridic oil. Some of the esters 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 6 carbon atoms or mono or dialkyl esters of citric acid or mixtures of mono, di and triesters of citric acid which are relatively high melting solids. While the glyceridic oil may be heated to dissolve some of these esters of citric acid, such heating, particularly if a high temperature is required, materially damages the oil for some purposes.

The compositions of this invention are prepared by dissolving the ester of citric acid or mixtures of ester in the solubilizing agent. The resulting compositions may then be added to a mass of an oil, such as a glyceridic oil. The resulting mixture may, if desired, be agitated at a suitable temperature, such as 40° to 60° C. The agitation readily disperses the composition uniformly throughout the mass of the oil and, as a consequence, a relatively homogeneous product is obtained.

The solubilizing agent must be capable of dissolving a material quantity of the ester or plurality of esters of citric acid at the temperatures at which the compositions are to be used. The solubilizing agent must also be miscible with the glyceridic oil or other oil to which the compositions of this invention are to be added. Moreover, from a practical standpoint the ultimate concentration of the solubilizing agent must not unduly contaminate the oil to which these compositions are added. For example, a large volume of a monocarboxylic acid, such as stearic acid, desirably should not be employed if the compositions are added to a glyceridic oil since it would materially increase the free fatty acid content thereof which would render the oil unsatisfactory for many purposes. However, the amount of the esters of citric acid required to impart the desired characteristics to an oil for most purposes may be added as a composition of this invention comprising the required ester of citric acid and the solubilizing agent without unduly increasing the free fatty acid content of the oil.

When the compositions of this invention are added to a glyceridic oil, even though the esters of citric acid, and particularly the mono and di-

esters of citric acid, are only slightly soluble therein, the esters are thrown out of the solubilizing agent in a finely divided state to form a liquesol and thereby present a very large surface in contact with the glyceridic oil. As a result, they are easily dispersed throughout the main body of the treated oil, and eventually dissolve especially when the main body of the oil is kept agitated.

Examples of the monocarboxylic acid monoesters of glycerol or propylene glycol or their polymers which may be employed as solubilizing agents are the monostearyl glycerides, monooleyl glycerides, monolauryl glycerides and monopalmityl glycerides, or their corresponding polyglycerol esters or mixtures thereof. These monocarboxylic acid monoesters, as commercially prepared, contain substantial amounts of the corresponding monocarboxylic acid diesters and small amounts of the corresponding monocarboxylic acid triesters. Such monocarboxylic acid monoesters as commercially prepared may be employed as the solubilizing agents in the compositions of this invention. Monoglycerides prepared from an edible oil, such as cotton seed oil, have been found to be very satisfactory solubilizing agents.

Examples of saturated monohydric 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.

Examples of the esters which may be employed in the compositions of this invention are the mono, di or triesters of citric acid derived from the following alcohols: n-propyl, isopropyl, n-butyl, crotyl, isobutyl, isoamyl, 2-ethylhexyl, lauryl, myristyl, palmityl, oleyl and stearyl.

Mixtures of monoaliphatic esters of citric acid, mixtures of dialiphatic esters of citric acid, mixtures of trialiphatic esters of citric acid, or mixtures of mono, di and trialiphatic 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 dissolved in the solubilizing agent. Or again, different monoalkylene esters of citric acid may be dissolved in the solubilizing agent; or a mixture of a monoalkyl ester and a monoalkylene ester may be employed.

Mixtures of various solubilizing agents may be utilized to effect uniform dispersion of the aliphatic esters of citric acid throughout the glyceridic oil. For example, a mixture of lauryl alcohol and cetyl alcohol may be employed to effect the solubilizing of monoisopropyl citrate in the glyceridic oil. Alternately, a mixture of different monocarboxylic acid monoesters of glycerol or propylene glycol may be utilized for the solubilizing of the esters.

The esters used in the compositions of this invention are prepared by the esterification of citric acid and a monohydric alcohol preferably in proportions which favor the formation of the mono, di or triesters whichever is predominantly desired. 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 the mono, 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. The di and triesters may be obtained in pure form, if desired, by following a similar procedure to that used in the production of the monoester by utilizing appropriate solvents. If desired, for some uses the esters need not be separated, but the entire reaction product including mono, di and triesters of citric acid may be dissolved in the solubilizing agent to form the composition of this invention.

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

Example 1.—Composition containing monoisopropyl citrate and monocarboxylic acid monoesters of glycerol

One gram of monoisopropyl citrate is dissolved in 5 grams of monocarboxylic acid monoesters of glycerol prepared from a winterized, refined unhydrogenated but deodorized corn oil. The monocarboxylic acid monoesters of glycerol are prepared from this corn oil by reacting glycerol 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 in the oil-coupling agent may be utilized to distribute the monoisopropyl citrate uniformly throughout a body of vegetable oil. For example, the solution may be 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 prepared as follows:

Equal parts of U. S. P. citric acid and commercial 99% 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 (about 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	Calcd.
Acid Value	454	480
Saponification Value	709	720

This product solidifies after long standing and and consists of a mixture of about 90% monoester and 10% diester. The resulting product,

without further purification, may be used to form the solution with an oil-solubilizing agent, such as the monocarboxylic monoesters of glycerine herein described.

Example 2.—Composition containing mono, di and triisopropyl citrates and monocarboxylic acid monoesters of glycerol

The composition of this example may be utilized for dispersing monoisopropyl citrate throughout a mass of a glyceridic oil, such as corn salad oil. The composition comprises monoisopropyl citrate together with the diisopropyl citrate and triisopropyl citrate and the monoglycerol ester 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 to be added. The monoisopropyl citrate, diisopropyl citrate and triisopropyl citrate and the monoglycerol esters are preferably mixed with a quantity of the oil being treated to form a homogeneous mixture. The mixture of esters is produced as follows:

260 grams of anhydrous citric acid are mixed with 130 grams of commercial 99% 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 1 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 glycerol.

A solution of the mixed isopropyl ester prepared as described herein is obtained by dissolving 38 grams of the mixed esters in 62 grams of monoglycerol esters of the fatty acid components of corn oil.

10 cc. of this solution 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. By this procedure, the mixed esters are dispersed uniformly throughout the mass of the corn oil.

Example 3.—Composition containing mono, di and triisopropyl citrates and oleyl alcohol

5 parts of mixed isopropyl citrate prepared in accordance with the procedure outlined in Example 2 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. The mixed isopropyl citrates are dispersed throughout the mass of the sunflower seed oil.

Example 4.—Composition containing mono, di and triethyl citrates and monocarboxylic acid monoesters of glycerol

Mono, di and triethyl citrate are dispersed uniformly throughout lard by a composition comprising monoethyl citrate, diethyl citrate, triethyl citrate and monoglycerol monoesters of the fatty acid components of the lard to which it is added. The monoethyl citrate, diethyl citrate, and triethyl citrate are prepared simultaneously by the method hereinafter described, and the mixture of mono, di and triethyl citrates is dissolved in the monoglycerol monoesters prepared from fatty acid components of the lard. 50 grams of the mixture of mono, di and triethyl citrates are added to 50 grams of the monoglycerol monoester. The monoglycerol monoesters are prepared in the same manner as the monoglycerol monoesters in Example 1. 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. Typical acid and saponification values of the resulting mixture are:

Acid value	258.2
Saponification value	680.7

Example 5.—Composition containing mono, di and triisopropyl citrates and oleic acid

One part of the mixed mono, di and triisopropyl citrates prepared in accordance with Example 2 are dissolved at a temperature of about 140° F. in 5 parts of oleic acid. The resulting composition is clear at that temperature and may be utilized for dispersing the mono, di and triesters throughout a body of a glyceridic oil. The solution of the mixed esters dissolved in the oleic acid was homogeneous at above 58° C. Below this point, cloudiness appeared which eventually would result in a two-layer separation. Desirably, therefore, the solution is added to the glyceridic oil above 58° C.

Example 6.—Composition containing relatively pure diisopropyl citrate and stearic acid

Relatively pure diisopropyl citrate was obtained from the mixed isopropyl esters obtained in accordance with the method described in Example 2, by the use of suitable solvents such as ethyl ether and petroleum ether. 40 parts of the resulting substantially pure diisopropyl citrate was dissolved at about 140° F. in 60 parts of stearic acid. This composition was homogeneous almost down to the solidification point of the mixture. If it is to be utilized to disperse uniformly the diisopropyl citrate throughout a mass of glyceridic oil such as corn oil, the composition should be added at a temperature above the melting point of stearic acid.

Example 7.—Composition containing mono, di and triisopropyl citrates and relatively pure propylene glycol stearate

10 parts of the mixed isopropyl citrates obtained in accordance with the method described in Example 2 are dissolved at a temperature of about

140° F. in 50 parts of relatively pure propylene glycol stearate.

Example 8.—Composition containing mono, di and triisopropyl citrates and lecithin

78 parts of the mixed isopropyl citrates prepared in accordance with Example 2 are dissolved at a temperature of about 140° F. in 124 parts of lecithin.

Example 9.—Composition containing 2-ethylhexyl acid citrate and sorbitol distearate

10 parts of 2-ethylhexyl acid citrate are dissolved at a temperature of about 140° F. in 10 parts of sorbitol distearate. The 2-ethylhexyl acid citrate is prepared in a manner similar to that described for the preparation of the isopropyl citrates in Example 2, by reacting citric acid with 2-ethylhexyl alcohol.

Example 10.—Composition containing lauryl acid citrate and diglycol laurate

10 parts of lauryl acid citrate are dissolved at a temperature of about 140° F. in 10 parts of diglycol laurate. The lauryl acid citrate is prepared by reacting citric acid with lauryl alcohol in a manner similar to that described for the preparation of the monostearyl citrate in Example 11, infra. The composition containing the lauryl acid citrate dissolved in diglycol laurate was homogeneous at 140° F.

Example 11.—Composition containing relatively pure monostearyl citrate and trioleyl citrate

10 parts of relatively pure monostearyl citrate were dissolved at a temperature of 140° F. in 30 parts of trioleyl citrate. The relatively pure monostearyl citrate was 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 cease 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).

The trioleyl citrate was prepared by reacting citric acid and oleyl alcohol in such proportions as to favor the formation of the trioleyl citrate. The composition containing the relatively pure monostearyl citrate and trioleyl citrate was clear and homogeneous when warm and suitable for adding to an oil.

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 composition of matter consisting essentially of an edible, oil-miscible vehicle having dissolved therein a monoester of citric acid selected from the class consisting of monoethyl citrate, monoisopropyl citrate, mono-n-propyl citrate, monocrotyl citrate, mono-n-butyl citrate, monoisobutyl citrate, monoisoamyl citrate, mono-2-ethylhexyl citrate, monolauryl citrate, monomyristyl citrate, monopalmityl citrate, monooleyl citrate and monostearyl citrate, the amount of said monoester being 15 to 37½% of said composition.

2. A composition of matter in accordance with claim 1, in which the edible, oil-miscible vehicle is monoglycerides of a fatty acid in which the fatty acid group has at least 10 carbon atoms.

3. A composition of matter in accordance with claim 1, in which the edible, oil-miscible vehicle is a monohydric aliphatic alcohol having at least 6 carbon atoms.

4. A composition of matter in accordance with claim 1, in which the edible, oil-miscible vehicle is a fatty acid having at least 10 carbon atoms.

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

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