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ANTIOXIDANT CONCENTRATES COMPRISING REACTION PRODUCTS OF MIXED GLYCERIDES AS SOLVENT CARRIERS

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16 Claims. (Cl. 252—399)

This invention relates to compositions useful as antioxidants for fats and oils, and more particularly to compositions for such use comprising alkylated hydroxyphenyl ethers, alkyl esters of gallic acid, synergistic acids or esters thereof and a solvent carrier comprising a reaction product of propylene glycol and mixed glycerides of normal and hydrogenated animal and vegetable fats and oils.

It has long been known that phenols such as hydroquinone, guaiacol, eugenol, gallic acid and its esters are useful antioxidants for fats and oils (Moureu et al. "Compt. rend" 174,288 (1922). It is also known that the phenolic compound such as the alkylated hydroxyphenyl ethers, for example, alkylated hydroxyanisoles, etc. can be used as antioxidants for fats and oils. It is further known that the antioxidant action of the named compounds can be synergized with acids, e. g. citric acid, o-phosphoric acid, tartaric acid, etc. While these phenolic compounds, as well as their synergistic combinations with acids of the above-mentioned kind, have been found to be adequately effective in retarding oxidative rancidity during the stroage of fats and oils, they are subject to the disadvantage in many instances of being only slightly and difficultly soluble in the fatty materials to which they are added. Since these antioxidants are solids rather than liquids, under normal conditions, it is advantageous to have a suitable solvent carrier such as, for example, propylene glycol to facilitate the solution of these active components in the fats and oils to be stabilized. If such a solvent carrier is not present, a considerable percentage of the effective amounts of the antioxidants are frequently either lost or occur in entirely too high concentrations because of incomplete solution and nonuniform distribution of the antioxidants throughout the fat or oil to be stabilized.

I have now found that the solution of mixtures of certain of these antioxidants in fats and oils can be materially improved if a concentrate of these antioxidants in a reaction product of propylene glycol with mixed glycerides of fatty acids, with or without added propylene glycol as a cosolvent, is employed. The use of this kind of reaction product, I have found, gives concentrates having materially lower cloud point and solidification temperatures than concentrates of the same kind, but devoid of such reaction products. Also my new concentrates containing the reaction product of propylene glycol and mixed glycerides, if solidified at freezer temperatures, recover or liquify more rapidly to true solutions when returned to room temperatures. All of the active components of the synergistic antioxidant combinations employed in my invention are readily dissolved over the range of concentrations contemplated by the reaction products of propylene glycol and the mixed glycerides, and the reaction products are themselves readily soluble in the various animal and vegetable fats or oils to be stabilized. For example, I have found that the solubilities of the said reaction products in cottonseed oil or in lard are equal to or, in some cases, slightly better than simple mechanical mixtures of propylene glycol and mixed glycerides. While propylene glycol has been used alone previously as a solvent carrier dissolving all the active components of the usual synergistic combinations over the range of concentrations generally employed, it has the disadvantage that it dissolves only with some difficulty in the fats and oils to be stabilized and thereby retards solution of the antioxidants in the fats and oils. Those of my new antioxidant concentrates containing as the solvent carrier a mixture of propylene glycol and the reaction product of propylene glycol and mixed glycerides are particularly well adapted for preparing certain antioxidant concentrates and stabilizing various animal and vegetable fats and oils. The glyceride-glycol ratio can vary within any limits, but preferably from 5 to 95% by weight of the reaction product to from 95 to 5% by weight of propylene glycol. However, all of my new concentrates remain liquid at temperatures as low as 15° F. and thus enables the fats and oils producer to add the concentrate directly to the fats and oils at any convenient stage during or after processing, and in many cases, without the necessity of heating or otherwise adjusting the temperature of the larger bulk of fats and oils to be stabilized. They also facilitate solution of the antioxidant at the ultimate consumer's plant by enabling him to easily dissolve the antioxidant concentrate in the fat or oil by a proportioning method with assurance that the active components will be completely and uniformly distributed throughout the fat or oil with a minimum of effort and expense.

It is, accordingly, an object of my invention to provide an antioxidant concentrate which is highly miscible with animal and vegetable fats and oils, and which facilitates greatly the solution of the active antioxidant components in such fats and oils. Another object is to provide an antioxidant solution which is liquid at ordinary storage temperatures. Another object is to formulate an effective synergistic antoxidant combination for the protection of animal and vegetable fats and oils against oxidative rancidity. Still another object is to provide a suitable solvent carrier comprising a reaction product of mixed glycerides and propylene glycol which readily dissolves all the active components such as alkylated hydroxyphenyl ethers, alkyl esters of gallic acid and synergizing acids. Other objects will become apparent from a consideration of the following description and examples.

According to my invention, I prepare my new concentrates by dissolving one or more alkylated hydroxyphenyl ethers and one or more gallic acid esters in a solvent carrier consisting of a reaction product of propylene glycol and mixed glycerides of an animal or vegetable fat or oil, or in a mixture of the reaction product and propylene glycol, preferably in the ratio of from 5 to 95% by weight of the reaction product and from 95 to 5% by weight of propylene glycol. Mixtures of reaction products derived from the mixed glycerides of different animal and vegetable oils and fats can be employed. In addition to the alkylated hydroxyphenyl ethers and the gallic acid esters, advantageously my new concentrates can contain a synergizing compound such as citric acid, monoisopropyl citrate, 2-hydroxypropyl citrate, o-phosphoric acid, tartaric acid and ascorbic acid. The concentrates of my invention also include an alkylated hydroxyphenyl ether, an alkylated hydroxyphenyl ether and a synergistic acid or ester, or a gallic acid ester and a synergistic acid or ester. Advantageously, the total weight of the alkylated hydroxyphenyl ether in the concentrate is from 3 to 50%, the total weight of the gallic acid ester in the concentrate is from 2 to 30% and the total weight of the synergizing compound is from 1 to 20%; based on the total weight of the concentrate, the remainder being the reaction product of propylene glycol and mixed glycerides alone or the reaction product plus propylene glycol. In no case, should the weight of the solvent carrier be less than 20 to 97% of the total weight of the concentrate.

Advantageously, the total weight of the alkylated hydroxyphenyl ether employed is from 0.5 to 5.0 times the

total weight of the gallic acid ester. Advantageously, the total weight of the synergizing acid or ester is from 0.2 to 1.0 times the total weight of the gallic acid ester.

The glycerides which I employ for preparing the reaction products employed in practicing my invention are mixtures in any combinations of mono-, di- and triglycerides, of edible animal and vegetable fats and oils such as lard, tallow, corn oil, cottonseed oil, coconut oil, peanut oil, soya oil, hydrogenated lard, hydrogenated soya oil, and the like. Such mixed glycerides can be prepared or compounded as described by N. H. Kuhrt in U. S. Patent 2,634,234, U. S. Patent 634,278 and U. S. Patent 2,634,279, all dated April 7, 1953. Such mixed glycerides are reacted with propylene glycol by heating a solution or mixture of propylene glycol and the desired glycerides, with or without a catalyst, to give the reaction products employed as a solvent carrier in my new antioxidant concentrates. Advantageously, the reaction is carried out in an inert atmosphere such as nitrogen, carbon dioxide, etc. The reaction is believed to be an ester interchange between the polyhydroxy alcohol and the mixed glycerides, but due to the complexity and the wide range of molecular sizes found in natural occurring glyceride esters, the exact chemical compositions of the reaction products are not known. The ratio of the reactants can vary between 1 and 3 moles of propylene glycol to 1 mole of the mixed glycerides. A ratio of approximately 5 parts by weight of mixed glycerides to 2 parts by weight of propylene glycol gives a particularly efficacious reaction product. The reaction temperature can vary from 100° to 180° C. and the reaction period from 1 to 8 hours. In general, the lower the temperature, the longer the time required for interchange of the fatty acids between the glyceride and the glycol. Although a catalyst is not necessary for this reaction, the presence of either alkaline or acid catalysts such as an alkali-metal hydroxide e. g. sodium hydroxide, potassium hydroxide, etc., o-phosphoric acid, an alkali-metal alkoxide e. g. sodium methoxide, sodium ethoxide, potassium ethoxide, etc. decrease the required temperature and the time of reaction. Since fats and oils are unstable in an alkaline medium, it is desirable to acidify those solvents prepared with an alkaline catalyst. The preferred catalyst is o-phosphoric acid, because it eliminates two operations, i. e. the neutralization of the alkaline catalyst and filtration to remove the salt formed.

The reaction products prepared in the above-described manner can readily be incorporated with the active antioxidant components, preferably as follows: The solvent consisting of the reaction product or the reaction product plus propylene glycol is heated and agitated at 80° C., the synergizing acid, if used, is sifted in first, the gallic acid ester is sifted in next, and finally the alkylated hydroxyphenyl ether is added. The time for complete solution of the antioxident components is approximately 15 minutes.

Some of the benefits attributed to the presence of the reaction product obtained by the processes of the above examples in a typical concentrate can be seen from the table below:

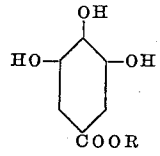
TABLE 1

[Reaction product of 5 parts corn oil mixed glycerides (containing 70 to 90% by weight of mono-glycerides) and 2 parts propylene glycol]

Cloud point (partial solidification of the higher molecular components, but still free flowing)[1]	19–30° F.
Solidification point (mushy solid, not free flowing)[1]	15–20° F.
Solubility of antioxidants at 75° F.:	
Butylated hydroxyanisole	Over 50%
Propyl gallate	Approx. 25%
Citric acid	Approx. 3%

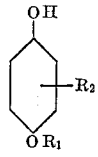
[1] Concentrate consisting of 77% by weight of the said reaction product, 14% by weight of butylated hydroxyanisole, 6% by weight of propyl gallate and 3% by weight of citric acid.

The gallic acid esters which I employ in practicing my invention are represented by the following general formula:



wherein R represents an alkyl group containing from 1 to 12 carbon atoms, e. g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tertiarybutyl, n-amyl, lauryl, etc. groups. Typical examples include methyl gallate, ethyl gallate, n-propyl gallate, isopropyl gallate, n-butyl gallate, isobutyl gallate, lauryl gallate, etc.

The alkylated hydroxyphenyl ethers which I employ in practicing my invention are represented by the following general formula:



wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms, and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms. Typical examples include, 2-tertiarybutyl-4-hydroxyanisole, 3-tertiarybutyl-4-hydroxyanisole, 2-tertiarybutyl-4-hydroxyphenetole, 3-tertiarybutyl-4-hydroxyphenetole, 2-tertiaryamyl-4-hydroxyanisole, 3-tertiaryamyl-4-hydroxyanisole, 2-tertiaryamyl-4-hydroxyphenetole, 3-tertiaryamyl-4-hydroxyphenetole, etc.

The alkylated hydroxyphenyl ethers above defined can be prepared by reacting p-hydroxyanisole or p-hydroxyphenetole with tertiary butyl or tertiary amyl alcohol, at a temperature of from 80 to 90° C., in the presence of phosphoric acid as a catalyst. The alkylated hydroxyphenyl ethers can also be prepared by reacting p-hydroxyanisole or p-hydroxyphenetole with isobutylene or with isoamylene, in the presence of sulfuric acid.

The following examples illustrate the manner for preparing the reaction products of the mixed glycerides and propylene glycol.

Example 1

0.330 g. of sodium hydroxide (equivalent to 0.10% based on the weight of glycerides) was dissolved in 132 g. of propylene glycol. To this solution was added 330 g. corn oil mixed glycerides (containing from 70 to 90% by weight of mono-glycerides and from 30 to 10% by weight of di-glycerides).

The mixture was purged with nitrogen for a period of about 15 minutes. And the inert atmosphere was maintained throughout the reaction period. The purged mixture was stirred and heated to 160° C. and held at this temperature for one hour. Then 0.475 g. (equivalent to 0.144% based on the weight of the glycerides) of o-phosphoric acid was added. The mixture was cooled under the atmosphere of nitrogen to about 30° C., diatomaceous earth (about 2% based on the total weight of the mixture) was added, and the resulting mixture filtered under vacuum to remove precipitated sodium phosphate and the diatomaceous residue.

Example 2

0.318 g. of 85% o-phosphoric acid (equivalent to 0.096% based on the weight of glycerides) was dissolved in 132 g. of propylene glycol. To this solution was added 330 g. of corn oil mixed glycerides (containing from 70 90% by weight of monoglycerides and from 30 to 10% by weight of di-glycerides). The mixture was purged with nitrogen, heated and agitated for one hour at 160° C., and then cooled to about 30° C. under a protective ni-

trogen atmosphere. Uniform solution or dispersion of the reaction mixture was maintained throughout the reaction by mechanical means.

Efficacious concentrates which can be prepared with the reaction products obtained by the processes of the above examples are set forth in the following examples:

Example 3

	Parts by weight
Reaction product of 5 parts corn oil mixed glycerides (containing from 70 to 90% by weight of mono-glycerides) and 2 parts propylene glycol	70
Butylated hydroxyanisole	20
n-Propyl gallate	6
Citric acid	4

Example 4

	Parts of weight
Same reaction product as Example 3	60
Propylene glycol	10
Butylated hydroxyanisole	18
n-Lauryl gallate	8
Citric acid	4

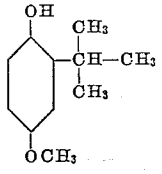
Example 5

	Parts of weight
Same reaction product as Example 3	90
Butylated hydroxyanisole	10

The above concentrates are of such compositions that one pound will provide adequate stability to 2000 pounds of fats and oils or fatty foods when properly incorporated in these materials. Such a concentrate is a homogeneous system at ordinary temperatures and lower. It is, therefore, capable of being manufactured and handled in ordinary channels of commerce without any separation of the components. All of the components of the synergistic combination are suitable for incorporation in edible products in concentrations much greater than result from the use of these mixtures.

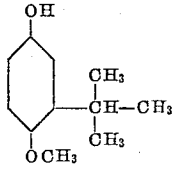
In the above examples, the n-propyl gallate and the n-lauryl gallate can be replaced by a like amount of any of the previously mentioned and suitable gallic acid esters, for example, by ethyl gallate, n-propyl gallate, isopropyl gallate, n-butyl gallate, etc., to give equally efficacious concentrates. Likewise, the butylated hydroxyanisole can be replaced by a like amount of any of the previously mentioned and suitable other alkylated hydroxyphenyl ethers.

The butylated hydroxyanisole employed in the above examples is a mixture of approximately equal parts by weight of



3-tertiarybutyl-4-hydroxyanisole

and



2-tertiarybutyl-4-hydroxyanisole

Instead of this mixture, an equal weight of either 3-tertiarybutyl-4-hydroxyanisole or 2-tertiarybutyl-4-hydroxyanisole can be employed, or an equal weight of 2-tertiarybutyl - 4 - hydroxyphenetole, 3 - tertiarybutyl-4-hydroxyphenetole, 2-tertiaryamyl-4-hydroxyanisole, 3-tertiaryamyl - 4-hydroxyanisole, 2-tertiaryamyl-4-hydroxyphenetole or 3-tertiaryamyl-4-hydroxyphenetole can be employed to give concentrates having generally similar stabilizing properties.

Example 6

	Parts by weight
Same reaction product as Example 3	55
Propylene glycol	22
Butylated hydroxyanisole	14
n-Propyl gallate	6
Citric acid	3

Example 7

	Parts of weight
Reaction product of 5 parts cottonseed oil mixed glycerides (containing from 70 to 90% by weight of mono-glycerides) and 2 parts propylene glycol	40
Propylene glycol	30
Butylated hydroxyanisole	20
Propyl gallate	6
Citric acid	4

The reaction product in above Example 7 can be prepared in similar manner as set forth in Example 2 by simply substituting an equal amount of cottonseed oil mixed glycerides in place of the corn oil mixed glycerides.

Example 8

	Parts by weight
Same reaction product as Example 3	55
Propylene glycol	22
Mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl - 4 - hydroxyanisole	14
n-Lauryl gallate	6
2-hydroxypropyl citrate	3

Example 9

	Parts by weight
Same reaction product as Example 7	70
Mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl - 4 - hydroxyanisole	20
n-Lauryl gallate	6
Monoisopropyl citrate	4

Example 10

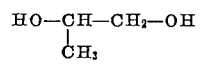
	Parts by weight
Same reaction product as Example 7	50
Propylene glycol	40
n-Propyl gallate	6
Citric acid	4

The antioxidant concentrates of my invention illustrated by the preceding examples are homogeneous systems even at temperatures as low as 0° F. Below 15–20° F., however, these solutions progressively solidify with decreasing temperature, but there is no separation of the active components from the solvent and rapid recovery to a true solution occurs when the concentrate is returned to temperatures 70° F. and above. All components of each formula shown can be replaced with the previously described alternate derivatives of the same class of compounds.

All of the aforementioned concentrates of my invention can be readily incorporated into animal and vegetable fats and oils, fatty acids and fat-containing foods such as, for example, tallow, lard, peanut oil, palm oil, coconut oil, cottonseed oil, soya bean oil, sunflower seed oil, sesame oil, hydrogenated oils and shortenings, stearic acid, bacon, etc., to protect these materials from oxidative rancidity. They can also be used to impregnate wrapping materials such as paper, cloth, etc. that are intended for enclosing foods. While a 0.05% concentration of the antioxidant solution, based on the weight of the material to be stabilized, appears to be ideally suited for incorporation into and for stabilization of the above mentioned materials, concentrations as low as 0.01% also will give satisfactory results for some purposes. Concentrations higher than 0.05% (up to 1.0%) also may be desirable for special uses. The concentrates are practically odorless, pale yellow in color

and do not discolor fats or oils to which they are added. Used in prescribed amounts, they are odorless and tasteless. They can be stored indefinitely without loss of antioxidant value. The concentrates can be dissolved in the fat or oil to be stabilized in any suitable container, such as a rolling drum or a mechanically agitated tank.

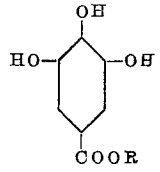
By the term "propylene glycol," I mean the compound which has the following formula:



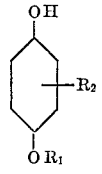
While my invention has been illustrated with the reaction products of corn oil mixed glycerides and cottonseed oil mixed glycerides with propylene glycol, with and without mechanically admixed propylene glycol, it will be understood that other of the mentioned animal and vegetable fats and oils containing mixed glycerides of mono-, di- and tri-glycerides, in various combinations are also operable solvent carriers, for the antioxidant concentrates of my invention containing an alkylated hydroxyphenyl ether, a gallic acid ester and a synergizing acid or ester.

What I claim is:

1. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of animal and vegetable fats and oils at a temperature of from 100° to 180° C., at least one gallic acid ester selected from those represented by the following general formula:

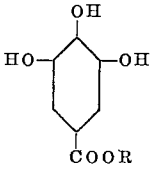


wherein R represents an alkyl group containing from 1 to 12 carbon atoms, and at least one alkylated hydroxyphenyl ether selected from those represented by the following general formula:

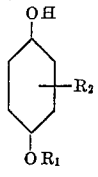


wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate and the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% by weight of the concentrate.

2. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., at least one gallic acid ester selected from those represented by the following general formula:

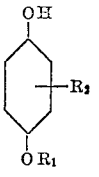


wherein R represents an alkyl group containing from 1 to 12 carbon atoms, at least one alkylated hydroxyphenyl ether selected from those represented by the following general formula:



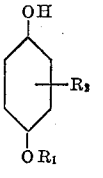
wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate, the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate and the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of the said reaction product being from 20 to 97% of the weight of the concentrate.

3. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., at least one alkylated hydroxyphenyl ether selected from those represented by the general formula:



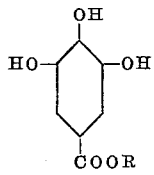
wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate and the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of mixed glycerides being from 30 to 96% of the weight of the concentrate.

4. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., and at least one alkylated hydroxyphenol ether selected from those represented by the genera formula:



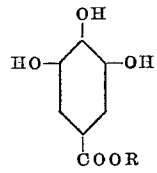
wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate, the weight of the mixed glycerides being from 50 to 97% of the weight of the concentrate.

5. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., and at least one gallic acid ester selected from those represented by the following general formula:



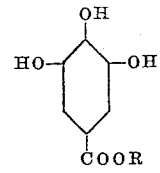
wherein R represents an alkyl group containing from 1 to 12 carbon atoms, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate, the weight of the mixed glycerides being from 70 to 98% of the weight of the concentrate.

6. An antioxidant solution consisting of the reaction product obtained by heating a mixture of from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., at least one gallic acid ester selected from those represented by the following general formula:

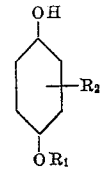


wherein R represents an alkyl group containing from 1 to 12 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of mixed glycerides being from 50 to 97% of the weight of the concentrate.

7. An antioxidant solution consisting of a mixture of propylene glycol and the reaction product obtained by heating from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., the ratio of the reaction product to propylene glycol being between 6:1 and 3:4, at least one gallic acid ester selected from those represented by the following general formula:

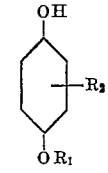


wherein R represents an alkyl group containing from 1 to 12 carbon atoms, at least one alkylated hydroxyphenyl ether selected from those represented by the folowing general formula:



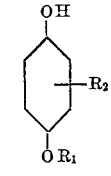
wherein R_1 represents an alkyl group containing from 1 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate, the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate and the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of the said mixture of propylene glycol and the said reaction product being from 20 to 97% of the weight of the concentrate.

8. An antioxidant solution consisting of a mixture of propylene glycol and the reaction product obtained by heating from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., the ratio of the reaction product to propylene glycol being between 6:1 and 3:4, at least one alkylate hydroxyphenyl ether selected from those represented by the following general formula:



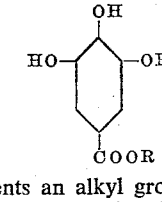
wherein R_1 reprents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the alkylate hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate and the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of the mixture of mixed glycerides and propylene glycol being from 30 to 96% of the weight of the concentrate.

9. An antioxidant solution consisting of a mixture of propylene glycol and the reaction product obtained by heating from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature from 100° to 180° C., the ratio of the reaction product to propylene glycol being between 6:1 and 3:4, and at least one alkylated hydroxyphenyl ether selected from those represented by the following general formula:



wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, the total weight of the alkylated hydroxyphenyl ether being from 3 to 50% of the weight of the concentrate, and the weight of the mixture of mixed glycerides and propylene glycol being from 50 to 97% of the weight of the concentrate.

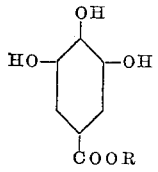
10. An antioxidant solution consisting of a mixture of propylene glycol and the reaction product obtained by heating from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a temperature of from 100° to 180° C., the ratio of the reaction product to propylene glycol being between 6:1 and 3:4, and at least one gallic acid ester selected from those represented by the following general formula:



wherein R represents an alkyl group containing from 1 to 12 carbon atoms, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate, the weight of the mixture of mixed glycerides and propylene glycol being from 70 to 98% of the weight of the concentrate.

11. An antioxidant solution consisting of a mixture of propylene glycol and the reaction product obtained by heating from 1 to 3 moles of propylene glycol and 1 mole of mixed glycerides of a vegetable oil at a tem-

perature of from 100° to 180° C., the ratio of the reaction product to propylene glycol being between 6:1 and 3:4, at least one gallic acid ester selected from those represented by the following general formula:



wherein R represents an alkyl group containing from 1 to 12 carbon atoms, and at least one synergizing compound selected from the group consisting of citric acid, monoisopropyl citrate and 2-hydroxypropyl citrate, the total weight of the gallic acid ester being from 2 to 30% of the weight of the concentrate, and the total weight of the synergizing compound being from 1 to 20% of the weight of the concentrate, the weight of the mixture of mixed glycerides and propylene glycol being from 50 to 97% of the weight of the concentrate.

12. An antioxidant solution consisting of 70 parts by weight of the reaction product obtained by heating a mixture of approximately 5 parts by weight of corn oil mixed glycerides and 2 parts by weight of propylene glycol, at a temperature of from 100° to 180° C., 20 parts by weight of a mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl-4-hydroxyanisole, 6 parts by weight of normal propyl gallate and 4 parts by weight of citric acid.

13. An antioxidant solution consisting of 60 parts by weight of the reaction product obtained by heating approximately 5 parts by weight of corn oil mixed glycerides and 2 parts by weight of propylene glycol, at a temperature of from 100° to 180° C., 10 parts by weight of propylene glycol, 18 parts by weight of a mixture of

2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl-4-hydroxyanisole, 8 parts by weight of normal lauryl gallate and 4 parts by weight of citric acid.

14. An antioxidant solution consisting of 40 parts by weight of the reaction product obtained by heating approximately 5 parts by weight of cottonseed oil mixed glycerides and 2 parts by weight of propylene glycol, at a temperature of from 100° to 180° C., 30 parts by weight of propylene glycol, 20 parts by weight of a mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl-4-hydroxyanisole, 6 parts by weight of normal propyl gallate and 4 parts by weight of citric acid.

15. An antioxidant solution consisting of 55 parts by weight of the reaction product obtained by heating approximately 5 parts by weight of corn oil mixed glycerides and 2 parts by weight of propylene glycol, at a temperature of from 100° to 180° C., 22 parts by weight of propylene glycol, 14 parts by weight of a mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl-4-hydroxyanisole, 6 parts by weight of normal lauryl gallate and 3 parts by weight of 2-hydroxypropyl citrate.

16. An antioxidant solution consisting of 70 parts by weight of the reaction product obtained by heating approximately 5 parts by weight of cottonseed oil mixed glycerides and 2 parts by weight of propylene glycol, at a temperature of from 100° to 180° C., 20 parts by weight of a mixture of 2-tertiarybutyl-4-hydroxyanisole and 3-tertiarybutyl-4-hydroxyanisole, 6 parts by weight of normal lauryl gallate and 4 parts by weight of monoisopropyl citrate.

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