ABSTRACT OF THE DISCLOSURE

Salad oil containing, as an inhibitor of solids deposition, 0.001-1% polysaccharide (2-15 saccharide units per molecule) at least one-half esterified with C12-C44 unsaturated fatty acid dimer and C14-C22 saturated fatty acid amido diester and amido dimer being in a ratio of 1:6 to 6:1.

This invention relates to improved salad oils and to a method for improving salad oils.

Oils which are suitable for salad use frequently are stored in refrigerators. The prolonged cooling of such oils to temperatures normally encountered in refrigerators, such as from about 40° F. to about 50° F., generally results in the deposition of crystalline material, usually solid triglycerides, from the oil. This material may appear in the form of a cloud, or as clusters of crystals, and is considered objectionable by the housewife. In general, the tendency to form solid glycerides in oils also adversely affects the suitability of the oil for use in mayonnaise emulsions. Mayonnaise emulsions prepared from such oils tend to be unstable at low temperatures and are more easily broken.

Frequently it is desirable to hydrogenate natural vegetable oils, such as soybean oil, in order to improve their oxidative stability; however, hydrogenation tends to produce oil components of decreased solubility at ordinary refrigeration temperatures.

Accordingly, the primary object of this invention is to provide a salad oil of improved resistance to solids precipitation at cold temperatures.

It has now been found according to the present invention that the storage time at low temperatures without clouding can be greatly extended for a given salad oil by dissolving therein from about 0.001% to about 1%, by weight, of a mixed polysaccharide ester of oleic acid dimer and palmitic acid, said polysaccharide having from 2 to about 15 saccharide units per molecule. The polysaccharide should be at least about one-half esterified, and the ratio of oleic acid dimer to palmitic acid in the ester preferably should be from about 1:6 to about 6:1. The esters can be prepared by simple esterification reactions well known to those skilled in the art by elimination of water in a reaction between a carboxy compound and a hydroxy compound. A preferred method which includes an intermediate methanolysis step is illustrated in the examples below.

The polysaccharides which can be used to form suitable esters in the practice of this invention include, by way of example, and not limitation: disaccharides such as sucrose, maltose, lactose, and melibiose; trisaccharides such as mannitoose and raffinose; tetrasaccharides such as stachyose; dextrins having from about 5 to about 15 saccharide units per molecule; and mixtures of the foregoing polysaccharides. These polysaccharides can be obtained from well-known sources such as those described in the co-pending application of Frederick R. Hugenberg and Edwin S. Lutton, U.S. Ser. No. 355,424.

In the mixed polysaccharide esters of this invention, the palmitic acid can be replaced with other long-chain saturated fatty acids and the oleic acid dimer can be replaced with other long-chain unsaturated fatty acid dimers with substantially equivalent results. For example, the long-chain fatty acids which can be used also include myristic, stearic and other long-chain, aliphatic, monobasic acids having from about 14 to about 22 carbon atoms such as those described in the co-pending application of Frederick R. Hugenberg and Edwin S. Lutton, U.S. Ser. No. 355,424.

The fatty acid dimers which can be used in the practice of this invention are long-chain, aliphatic, dibasic acids having from about 28 to about 44 carbon atoms in the molecule. They are generally obtained from unsaturated fatty acids having from about 14 to about 22 carbon atoms which can be polymerized to form dimers. For example, linoleic acid can be polymerized by heating to form linoleic acid dimer as follows:

\[ \text{CH}_2(\text{CH}_2)\text{CH}==\text{CH}-\text{CH}-(\text{CH}=\text{CH})_2\text{COOH} \xrightarrow{\Delta} \]

\[ \text{CH}_2(\text{CH}_2)\text{CH}==\text{CH}-\text{CH}=(\text{CH}=\text{CH})_2\text{COOH} \]

\[ \text{CH}_2(\text{CH}_2)\text{CH}==\text{CH}-(\text{CH}=\text{CH})_2\text{COOH} \]

Common examples of such polymerizable acids are those containing two or more double bonds (polysaturated acids) such as the octadecadienoic acids containing two double bonds, for example, the above-mentioned linoleic acid, and the octacatrienoic acids containing 3 double bonds, for example, linoleic and eleostearic acids.

Other common polymerizable unsaturated acids having from about 14 to about 22 carbon atoms which can be used in the practice of this invention are octadecatrienoic acid (e.g., linic acid), octadeca tetraenoic acid (e.g., parinaric acid), eicosadienoic acid, eicosatrienoic acid (e.g., arachidonic acid), eicosapentaenoic acid, and clupanodononic acid. Monoensaturated fatty acids, such as oleic, elaidic and erucic acids also can be used to form suitable long-chain fatty acid dimers which can be used in the practice of this invention.

As an example, an ideal starting material for the preparation of linoleic acid dimer is pure linoleic acid. It will be appreciated, however, that the acids employed occur in nature as complex mixtures and isolation of pure linoleic acid is, as a practical matter, commercially unfeasible. Instead, sources rich in linoleic acid (generally 30% to 80%) are employed as starting acids.

One analytical method for describing mixtures of fatty acids having sufficient double bond functionality, to be readily polymerizable by conventional means is by reference to the iodine value (I.V.), i.e., the number of grams of iodine equivalent to the halogen absorbed by a 100 gram sample. In general, acid mixtures having iodine values of at least 120 will have sufficient double bond functionality to readily form the preferred long-chain fatty acid dimers by conventional means.

Illustrative of natural sources which are rich in linoleic acid are soybean oil, cottonseed oil, peanut oil, corn oil, sesame seed oil, sunflower seed oil, safflower oil, linseed oil and perilla oil. Oiticica oil is a particularly good source of linic acid and tung oil contains a high concentration of eleostearic acid. Fish oils, such as herring, mackerel, pilchard, salmon, and sardine oil also are suitable sources of polymerizable acids, particularly the higher fatty acids such as arachidonic and clupanodononic acids. Other oils such as tall oil, dehydrated caster oil, olive oil and rapeseed oil also contain significant proportions of suitable unsaturated acids. For example, olive oil is rich in oleic acid and rapeseed oil is rich in erucic acid.

The long-chain fatty acid dimers of this invention can be prepared by various methods known to those skilled in the art. For example, fatty oils containing substantial
amounts of glycerides of the above-mentioned polyunsaturated acids can be polymerized by thermal treatment. The process is accelerated by the presence of polymerization catalysts. The polymeric glycerides thus formed can be converted to the polymeric acids, for example, by hydrolysis.

Another method for the preparation of long-chain fatty acid dimers comprises subjecting the fatty oils to monohydrate with monohydric alcohols such as methanol and ethanol, thereby converting the glycerides of the unsaturated acids to the corresponding monooesters. The monooesters can be polymerized as above to yield esters of polymeric acid, from which the free polymeric acids can be obtained by hydrolysis.

Still another method for the preparation of long-chain fatty acid dimers comprises producing the free unsaturated fatty acids by hydrolysis of the fatty oils, followed by polymerization of the acids.

In the course of any of the above methods of preparation, the polymeric acids can be further purified or fractionated by any suitable means such as by distillation, crystallization or solvent extraction.

A preferred method of polymerizing the unsaturated fatty acids to form long-chain fatty acid dimers is described in U.S. Patent 2,482,761, granted to Goebel, Sept. 27, 1949, and comprises heating a polyunsaturated fatty acid at an elevated pressure and a polymerizing temperature of at least about 260°C, in the presence of a small amount of water.

Suitable methods for the polymerizing of monounsaturated fatty acids to form long-chain fatty acid dimers are described in U.S. Patent 2,731,481, granted to Harrison et al., Jan. 17, 1956, and U.S. Patent 2,792,519, granted to Barrett et al., May 21, 1957.

It will be appreciated that the polymerization methods generally employed will produce some trimer as well as the desired dimer. For example, a typical commercially available long-chain fatty acid dimer prepared from oleic or linoleic acid will contain from about 70% to 90% dimer, from about 10% to 30% trimer, and even traces of monobasic oleic or linoleic acid from which the dimer is derived. It should be understood that such mixtures or mixtures containing even higher proportions of trimer can be used in the practice of this invention.

The monooacylcholistic esters of this invention also contain a portion of short-chain fatty acid radicals, such as acetic and propionic fatty acid radicals, and a portion of long-chain unsaturated fatty acid radicals, such as oleic and linoleic fatty acid radicals, such as those described in the co-pending application of Frederick H. Hugenberg and Edwin S. Linton, U.S. Ser. No. 355,424, provided that the herein-described proportions of long-chain saturated fatty acids and long-chain unsaturated fatty acid dimers are also used to esterify the polyvalerate.

A wide variety of oils can be used as base oils which can be made resistant to deposition of high-melting solids at low temperatures in accordance with this invention. Included among suitable oils are the so-called natural salad oils such as olive oil, sunflower seed oil, safflower oil and sesame seed oil. Oils such as cottonseed oil and corn oil preferably are given a preliminary “winterizing,” degumming, or similar other treatment to remove the higher-melting solids to form a good base salad oil. Other oils, such as soybean oil, may require some hydrogenation to improve resistance to oxidative deterioration with prolonged storage, and the higher-melting glycerides formed during this hydrogenation treatment preferably are removed by winterization. Base salad oils can also be formed by directed, low-temperature interesterification or rearrangement of animal or vegetable fatty material, followed by removal of higher-melting glycerides formed during the reaction. See, for example, U.S. Patent 2,442,352, granted to E. W. Eckerly, June 1, 1948. Another group of oils includes those in which one or more short chain or lower fatty acids having from 2 to about 6 carbon atoms, such as acetic and propionic acids, replace in part, the longer chain or higher fatty acids present in natural triglyceride oils. Other base salad oils will suggest themselves to those skilled in the art, provided they have a suitable chill test as hereinafter defined. The base salad oils can be used individually or as mixtures of oils. As used herein, the term “base salad oil” is intended to include all such salad oil which will not form solids immediately when cooled to 30°F.

The procedure for measuring the resistance of salad oils to clouding and the critical inhibiting activity of the esters as used hereinafter involves preheating the oil or oil with inhibitor to a temperature of about 140°F, then cooling a 100 gram sample with air having a temperature of about 30°F until solids form in the oil or oil with inhibitor. As used herein, the term “chill test” is intended to define the total length of time of cooling with air having a temperature of 30°F until such solids form.

The ester and the base salad oil can be mixed together in any convenient manner. For example, the ester in liquid form can be mixed with the oil. If the ester is in solid form, it can be dissolved in the oil, although it may be desirable to heat the oil or the mixture of the oil and ester to facilitate solution.

The following examples will serve to further illustrate the invention. However, it should be understood that the invention is not limited to these illustrative examples.

Example 1

Commercial oleic acid dimer (Empol 1018) (500 grams) is refluxed with methanol (1000 cubic centimeters) for 2 hours using sulfuric acid catalyst (10 grams) to form the methyl ester of oleic acid dimer. The crude methyl ester is washed with 5% K_2CO_3 solution and with water and then dried under vacuum. Sucrose (11 grams) is heated with dimethylformamide (100 cc.) to 60°C to homogenize. The above methyl ester of oleic acid dimer (43 grams), “Triton B*-40% benzyl trimethylammonium hydroxide in methanol (10 cc. cubic centimeters), and cyclohexane (100 cubic centimeters) are added to the sucrose and dimethylformamide mixture, and the methyl alcohol is driven off over a period of 3 to 4 hours at 90°C. The above-formed sucrose ester of oleic acid dimer (30 grams) is refluxed with palmitoyl chloride (30 grams) in the presence of cyclohexane (100 cubic centimeters) and pyridine (10 cubic centimeters) for about one hour to form a mixed sucore ester of oleic acid dimer and palmitic acid (sucrose containing on the average about 10% esterified with oleic acid dimer and palmitic acid in a 1:1 ratio). The mixed sucrose ester at a concentration of 0.1%, by weight, in winterized cottonseed oil (having a chill test of 12 hours) extends the chill test of the winterized cottonseed oil to greater than 50 hours.

Example 2 is repeated except that, in Example 1 partially hydrogenated and winterized soybean oil (Iodine Value 107) is substituted for winterized cottonseed oil in an equal amount; in Example 3 raffinose is substituted for sucrose in an equivalent amount; in Example 4 steroyl chloride is substituted for palmitoyl chloride in an equivalent amount; in Example 5 linolenic acid dimer containing about 25% triglycerin is substituted for oleic acid dimer in an equivalent amount; in Example 6 one-fourth of the palmitoyl chloride is replaced with an equivalent amount of oleyl chloride and another one-fourth is replaced with an equivalent amount of acetyl chloride; in Example 7 the ratio of oleic acid dimer to palmitic acid in the mixed ester is changed to 1:3; in Example 8 the ratio of oleic acid dimer to palmitic acid in the mixed ester is changed to 3:1; and, in Example 9 the concentration of the mixed ester is changed to 6.05%. In these Examples 2 through 9, the improvements in chill test obtained with the mixed esters are substantially equivalent to the results obtained in Example 1.

If too large an amount of inhibitor is present in the
salad oil, it will be precipitated out of the oil as the oil-inhibitor mixture is cooled and possibly even promote crystallization of high-melting solids in the oil. Too small an amount of inhibitor, of course, will be relatively ineffective. Amounts of ester in excess of 1%, by weight, are unnecessary as affording no significant added improvement of the oil; and it is preferred to use from about 0.05% to about 0.1%.

What is claimed is:

1. A clear glyceride salad oil having improved resistance to deposition of high-melting solids and comprising a base salad oil having dissolved therein from about 0.001% to about 1%, by weight, of a mixed polysaccharide ester of oleic acid dimer and palmitic acid, said polysaccharide having from 2 to about 15 saccharide units per molecule and being at least one-half esterified, and said oleic acid dimer and palmitic acid being in a ratio of from about 1:6 to about 6:1.

2. The clear glyceride salad oil of claim 1 in which the polysaccharide is sucrose.

3. The clear glyceride salad oil of claim 1 in which the polysaccharide is raffinose.

4. The clear glyceride salad oil of claim 1 in which the base salad oil is derived from cottonseed oil.

5. The clear glyceride salad oil of claim 1 in which the base salad oil is derived from hydrogenated soybean oil.

6. The clear glyceride salad oil of claim 1 in which the mixed polysaccharide ester is present in an amount of from about 0.05% to about 0.1%, by weight.

7. A clear glyceride salad oil having improved resistance to deposition of high-melting solids and comprising a base salad oil having dissolved therein about 0.1% sucrose completely esterified with oleic acid dimer and palmitic acid in a ratio of about 1:1.

8. A clear glyceride salad oil having improved resistance to deposition of high-melting solids and comprising a base salad oil having dissolved therein from about 0.001% to about 1%, by weight, of a mixed polysaccharide ester of long-chain unsaturated fatty acid dimer having from about 28 to about 44 carbon atoms in the dimer and long-chain saturated fatty acids having from about 14 to about 22 carbon atoms, said polysaccharide having from about 2 to about 15 saccharide units per molecule and being at least one-half esterified, and said unsaturated fatty acid dimer and saturated fatty acid being in a ratio of from about 1:6 to about 6:1.

9. A clear glyceride salad oil having improved resistance to deposition of high-melting solids and comprising a base salad oil having dissolved therein about 0.1% sucrose completely esterified with long-chain unsaturated fatty acid dimer having from about 28 to about 44 carbon atoms in the dimer and long-chain saturated fatty acids having from about 14 to about 22 carbon atoms in a ratio of about 1:1.

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