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POLYETHYLENE GLYCOL ESTERS IN FAT

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The present invention is directed to polyethylene glycol esters, and more particularly to materials having utility in connection with fatty materials, such as edible fats and oils.

For a number of years there have been on the market certain mono- and di-esters of higher fatty acids and glycerine. Among such compounds were distearate and monostearate of glycerine, and monoesters of glycerine and saturated and unsaturated fatty acids. Such materials had been incorporated in edible oils and fats in minor proportions, such as the hydrogenated shortenings, lard or synthetic compositions of this general type in order to improve the properties of such shortenings for various culinary uses. All of the compounds so added had free or unesterified hydroxy groups on the glyceryl radical together with relatively long carbon chain of the acid component so that the compounds were relatively soluble in the fat, but at the same time they had hydrophilic groups, namely, OH groups, which would impart to the shortening emulsifying properties.

To a certain extent the desired results were accomplished by such compounds but it was found that when a shortening of this type was used for frying purposes, it had a great tendency to smoke at relatively low temperatures, which rendered it quite objectionable for the purpose. Also, in order to obtain adequate emulsifying effects, it was necessary to add relatively large quantities thereof to the shortening or the like. In so-called high ratio products wherein more sugar than flour is used, such a shortening has found a considerable market, but it required relatively large amounts of the mono- and diglycerides therein to obtain the desired result. It was necessary to add 5% or more of such compound in order to obtain good results as a high ratio shortening.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in products of the character described, it being among the objects of the present invention to provide a series of new compounds which may be used as such or which may be made into shortening, which does not depend on free hydroxy groups for providing adequate improved properties to the shortening, and which is eminently suitable for the purpose.

It is also among the objects of the present invention to provide a composition containing such a constituent which is capable of use in the culinary arts for all purposes, including baking, frying, and in high ratio shortenings.

It is further among the objects of the present

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invention to provide a composition for introduction into vegetable and animal oils and fats which will provide an effectiveness far greater than that of the free hydroxyl containing emulsifiers previously used.

It is still further among the objects of the present invention to provide a highly efficient agent in a shortening composition, whether liquid or solid, which will permit the same to be used for frying purposes without emitting any substantial amount of smoke at relatively high operating temperatures.

In practicing the present invention there is provided a series of esters of a polyethylene glycol having a molecular weight of at least 300. Better results are obtained with the higher molecular weight polyethylene glycols such as those having from 1000 to 2000 molecular weight and even higher, up to 4000. In general, the molecular weight of the polyethylene glycol is such that there are from 5 to 60 ethylene glycol radicals in the molecule.

Such a glycol is esterified with a fatty acid having at least 12 carbon atoms and up to the highest fatty acid found in vegetable and animal oils. Usually the amount of such fatty acid used in the reaction is sufficient to form the mono-ester of the glycol. The other hydroxy group of the glycol is esterified with a lower fatty acid having from 2 to 4 carbon atoms, namely, acetic, propionic and butyric acids and their isomers, so that the final products are substantially free from unesterified OH radicals.

In some cases, the higher fatty acid, which may be saturated or unsaturated or may be a mixture of such fatty acids, is reacted in such quantities with the glycol that a di-ester is formed. This has substantial value as an improving agent in shortenings.

The following are specific examples of the operation of the present invention.

Example 1

The starting material is polyethylene glycol having an approximate molecular weight of 1370, consisting of approximately 31 ethylene glycol radicals. 685 grams, equal to $\frac{1}{2}$ mol. of the glycol, is mixed with 140 grams of commercial stearic acid obtained from hydrogenated soya bean oil and having an iodine number of 2, being about $\frac{1}{2}$ mol.

The mixture is placed in a closed vessel connected to a vacuum pump and it is heated gradually to a temperature of 225° C. with continuous agitation and with the introduction of a flow of nitrogen to act as a blanket in the vessel.

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The vacuum is increased during the heating cycle so that when the temperature has reached 225° C. in about six hours, the pressure is from 5 to 10 millimeters mercury absolute. At such temperature, heating is continued and the vacuum is maintained until the percentage of free fatty acid has dropped below 4. Water is removed continuously during the operation and upon completion of the reaction, the product is allowed to cool to about 135° C.

Thereupon there is added to the reaction product, which is substantially the polyglycol monostearate, 60 grams of acetic anhydride (98%), equivalent to slightly over 1.2 mols. Heating is resumed and continued until the temperature has reached 200° to 210° C. A reflux condenser is provided so as to condense the vaporized acetic anhydride, which is returned for further reaction. The refluxing is continued for about one hour, or until substantially complete esterification with the acetic anhydride has taken place.

The resulting product is then usually treated to remove any residual acetic anhydride and acetic acid present by means of steam or by application of vacuum at elevated temperature. The resulting product may be filtered to remove suspended matter and cooled to room temperature. The diester so formed is a waxy solid, soluble in vegetable and animal oils and fats and has a melting point of 38° to 42° C.

Example 2

140 grams of oleic acid, equivalent to ½ mol., are placed in a suitable reaction vessel. About ½% of sodium hydroxide in 50% aqueous solution is added to the oleic acid to act as a catalyst in the reaction. The oleic acid is heated to 160° C., and ethylene oxide is bubbled into the reaction vessel under the surface of the liquid, preferably with continual stirring, but without any vacuum or pressure. The rate of addition is such that the ethylene oxide is fully absorbed. This is continued until about 255 grams of ethylene oxide has been introduced. The reactions which take place include the formation of a polymerized ethylene glycol, and at the end of the operation, the polyethylene glycol formed has a molecular weight of about 600 and is equivalent to ½ mol. At the same time under the temperature conditions, the mono-oleate of the polyethylene glycol has been formed.

There is then added to the product about 80 grams of propionic anhydride and esterification is caused to take place similarly to the second step of Example 1. The resulting product may be steam refined and filtered, giving the propionic-oleic ester of polyethylene glycol 600.

The products of Examples 1 and 2 described above may be added to a hydrogenated cottonseed shortening in small amounts, as from .05% to 0.2% with solution of the di-ester in the triglyceride. In such quantities the resulting shortening has a high degree of creaming quality and has been found suitable for general culinary purposes. In cake making, it imparts fluffiness to the baked product and the cake remains fresh for a longer period of time. In frying, as for instance in the making of potato chips, it has proven to have a high smoke point so that rapid frying of various foods is obtained in a satisfactory manner at a relatively high temperature without the formation of smoke or discomfort to the operator. In high ratio shortenings from 0.2% to 1.0% of the di-esters added to the fat is sufficient to provide a shortening which can

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be used in making high ratio baked products. Additional quantities of the di-esters may be introduced and up to 3% thereof has given excellent results. If desired, an amount up to 5.0% may be used but generally this has been found to be unnecessary. It has been found that 1% of many of the di-esters of the present invention are the equivalent of about 5% of glycerol monostearate previously used in high ratio shortening.

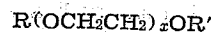
The present di-esters may be mixed with vegetable oils or animal oils as well as with the solid fats and the resulting products have similar properties for frying, cooking and baking purposes. The products are non-toxic and have a good flavor and odor. In the claims the term "edible fat" is intended to include the liquid as well as the solid fats.

Although the invention has been described setting forth several specific embodiments thereof, the invention is not to be limited to the specific examples as they were given for the purpose of illustrating the invention and not limiting it. Various changes in the details of the invention may be made within the spirit thereof. For instance, the temperature, pressure and other conditions of the operation may be considerably varied in accordance with usual practice in order to give the desired esterification results. The proportions of the polyglycol and the various fatty acids used may vary substantially from the exact amounts herein stated. It is not necessary that there be exactly one higher fatty acid and one lower fatty acid in each molecule but a variation wherein there is slightly more than one molecule on the average of the higher or lower fatty acid, still gives good results. While outside limits of proportions of the di-esters in oils and fats has been given, one may vary from these proportions to some slight extent but such variation does not give any materially better effects. Mixtures of the di-esters of the present invention with the emulsifying agents of the prior art may be incorporated in shortenings and the like.

These and other changes may be made within the principles herein set forth and the invention is to be broadly construed except as limited by the claims appended hereto.

I claim:

1. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a fatty acid radical having at least 12 carbon atoms, R' is a fatty acid radical having 2 to 4 carbon atoms, and x is a whole number from 5 to 60.

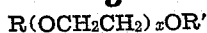
2. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a saturated fatty acid radical having at least 12 carbon atoms, R' is a fatty acid radical having 2 to 4 carbon atoms, and x is a whole number from 5 to 60.

3. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:

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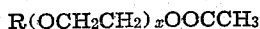
wherein R is an unsaturated fatty acid radical having at least 12 carbon atoms, R' is a fatty acid radical having 2 to 4 carbon atoms, and x is a whole number from 5 to 60.

4. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a fatty acid radical having at least 12 carbon atoms, and x is a whole number from 5 to 60.

5. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a saturated fatty acid radical having at least 12 carbon atoms, and x is a whole number from 5 to 60.

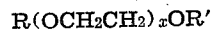
6. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein x is a whole number from 5 to 60.

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7. A composition of matter consisting essentially of an edible fat having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a fatty acid radical having at least 12 carbon atoms, R' is a fatty acid radical having 2 to 4 carbon atoms, wherein $(OCH_2CH_2)_x$ has a molecular weight of 1000 to 2000.

8. A composition of matter consisting essentially of shortening having incorporated therein from 0.05% to 5.0% of a compound taken from the class consisting of polyethylene glycol esters having the following general formula:



wherein R is a fatty acid radical having at least 12 carbon atoms, R' is a fatty acid radical having 2 to 4 carbon atoms, wherein $(OCH_2CH_2)_x$ has a molecular weight of 1000 to 2000.

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