1

3,353,964 CORANDOMIZED MARGARINE OILS Paul Seiden, Burlington, Ontario, Canada, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio No Drawing. Filed Aug. 21, 1964, Ser. No. 391,293 Claims priority, application Canada, Sept. 23, 1963, 885,132, Patent 718,373 5 Claims. (Cl. 99—118)

The present invention relates to the preparation of margarine oil and, more particularly, to margarine oil containing corandomized triglycerides of certain short chain and long chain fatty acid in proportions and amounts which impart improved properties to the marga- 15 rine oil and, consequently, to margarine prepared therefrom.

One preferred aspect of this invention relates specifically to an additive for margarine oil which is a corandomized blend of hydrogenated rapeseed oil with 20 coconut and/or palm kernel oil. Another particularly preferred aspect of this invention relates to a special margarine oil comprising a mixture of hydrogenated rapeseed oil, palm oil and coconut oil, which mixture is then corandomized.

Margarine consists of an emulsion of two phases, one of these being fatty in nature while the other is aqueous in nature. The physical characteristics of a finished margarine such as firmness, spreadability, and ease of melting in the mouth, are to a large extent determined by the characteristics of the oil, or fatty, constituent which makes up the fatty phase of the emulsion. These characteristics are to a large extent dependent on the percentages of the fatty matter which exist in the solid state at the various temperatures normally encountered during the 35 storage, use and consumption of the margarine.

For example, the margarine should melt readily in the mouth to avoid a sensation of "waxiness" or "stickiness" and to have a satisfactory flavor. This means there must be almost no fatty material in the solid state at or near body temperatures. On the other hand, at temperatures of use it must be capable of being spread and this requires that some portion of the fatty material be in the solid state at that temperature, but not so much that the margarine is hard and difficult to spread and not so 45 little that the margarine will "slump" or lose its shape.

In addition, it is usually preferred to produce a margarine product that duplicates or approaches the characteristics of butter. In general, however, margarines are formulated to have better physical stability at high temperatures than butter and therefore can be stored in both refrigerated or non-refrigerated storage. In specific cases margarines can be produced deliberately different from butter in other characteristics; i.e. margarines can be made spreadable at refrigerated temperature.

When some margarines are heated above about 70° F., part of their liquid oil content may start to seep or "oiloff" from the body of the margarine to the lower surfaces. This seepage increases with increase in temperature. If it becomes excessive, liquid oil can leak through the parchment wrap, soiling it as well as the outside carton and case. In addition to making the package unsightly and oily to the touch, the oil is more susceptible to rancidity because of the greater exposure of the oil to the air. Further, since margarine contains an aqueous phase, bacterial or mold contamination can also occur.

It is generally recognized therefore that margarines must have sufficient heat resistance to resist oil-off under trade conditions.

a margarine is to increase the higher melting saturated or trans fatty acid glyceride content by further hardening 2

the margarine oil. However such an increase, though improving the heat resistance of the margarine, results in an increased solids content and hence a significant loss in the eating quality or "melt in the mouth characteristics" of the margarine.

The solids content referred to hereinabove is expressed, at different temperatures, in terms of a "Solid Contents Index" (SCI) which is measured by what is essentially the test described in The Journal of the American Oil Chemists' Society, March 1954, volume XXXI, pages 98-103. The test involves a dilatometric measurement of the amount by which a fat expands when heated from a specific temperature to complete melting. Since this expansion is due to both a volume increase when solids change to liquids without a temperature change and a volume increase due to thermal expansion without change in phase from solid to liquid, allowance is made for the thermal expansion so that the change in volume gives a measure of the amount of solid phase present at the temperature of measurement. The test has been modified in that readings are taken after 30 minutes at the temperature of measurement.

SCI data for an oil are usually presented in the form of a curve in which the SCI is plotted against temperature. It is readily apparent that a flat SCI curve is undesirable for a margarine oil since it is necessary to have a change within a small temperature range from a plastic material to one that is essentially a liquid.

One feature of the present invention is the addition to margarine oils of an additive which while providing improved heat resistance tends to cause only a small increase in the solids content. By this feature, a margarine can be obtained which sacrifices far less eating quality than has been the case in the past. Since there is a definite relationship between the heat resistance, eating quality or "melt in the mouth characteristics" and spreadability properties of margarine, it is possible, by the present invention, to produce margarine with better eating qualities and/or spreadability particularly for use in colder geographic areas where less heat resistance is required. Thus, the present invention makes it possible to provide other improvements in addition to an improvement in heat stability.

In formulating margarine, soft oils can be hydrogenated and blended to provide good performance characteristics in eating quality, heat resistance, and spreadability. These soft oils include soybean oil, cottonseed oil, corn oil, sunflower oil, and peanut oil. However, certain other oils, particularly palm oil, coconut oil, and palm kernel oil generally cannot be used as major components in a blended margarine (that is, in an uninteresterified or non-randomized margarine) since, when mixed with soft oils, they tend to harm the performance characteristics of the margarine, particularly the heat resistance and eating quality. Therefore, use af palm oil, coconut oil, and palm kernel oil in margarine has been very limited.

At certain times and in certain geographical areas it may be economically desirable to use a mixture of palm oil and coconut oil as a major constituent of a margarine 60 oil. One of the advantages of this invention is that it provides a means for using such a mixture of oils in margarine.

By another feature of the present invention, margarine formulations can be developed having increased quantities 65 of palm oil, coconut oil, and/or palm kernel oil. Thus, greater flexibility in formulation can be achieved and high quality margarines can be composed with economically priced components depending on fluctuations in oil prices.

While some of the advantages and features outlined The conventional way of improving heat resistance of 70 above may be achieved through the use of the technique provided by co-pending application Ser. No. 236,416 filed Nov. 8, 1962, now Patent No. 3,298,837, it has now

been found that such technique may be improved in order to provide a better balance of eating quality versus heat stability for a wide variety of margarine formulations. Thus, in order to obtain a given heat stability, the use of the improved additive of the present invention in a margarine oil formula also provides improved eating quality compared to previous margarine formulations. Conversely, in order to obtain a given eating quality, the use of the improved additive of the present invention provides a better heat stability in a margarine compared to previous margarine formulation.

While it is a principal feature or object of the present invention to provide a margarine oil for preparing margarine having improved heat resistance, it is another feature of the present invention to provide a margarine oil for producing margarine having improved spreading char-

acteristics at low temperatures.

Still another object of the present invention is the provision of a margarine oil containing a soft oil, for example, soybean oil, and palm oil in which more palm oil is incorporated than heretofore possible to yield a margarine of improved quality.

Yet another object of the present invention is the provision of a margarine oil containing coconut oil and palm kernel oil in which more coconut oil is incorporated than heretofore possible to yield a margarine of improved

A still further object of the present invention lies in the provision of a margarine oil whereby a margarine is prepared having improved polymorphic crystal stability; in other words, a margarine is made more resistant to texture changes and physical breakdown due to change in the type of fat crystals.

A further object of the present invention lies in the provision of a margarine oil whereby a margarine is prepared having an improved balance of eating quality

versus heat stability.

A still further object of the present invention lies in the provision of a margarine oil whereby a margarine having good quality and heat stability is prepared from higher levels of palm oil and coconut oil than has heretofore been possible.

In its broad aspects the present invention provides a margarine oil adapted to be manufactured into a margarine of good spreadability, oil-off, slump and eating qualities, the margarine oil comprising at least about 5% by weight of corandomized triglycerides containing saturated short chain fatty acids having from 6 to 14 carbon atoms and saturated long chain fatty acids having from 20 to 22 carbon atoms, the amount of the saturated long chain fatty acids being about 0.3 to about 5% by weight of the margarine oil and the ratio of the saturated short chain fatty acids in the margarine oil to the saturated long chain fatty acids in the margarine oil being from are present in the margarine oil below about 0.3% by weight of the oil, there is a beneficial effect but it is very small and of no practical importance. Above about 5% by weight of the margarine oil, little additional practical improvement is found in the margarine attributable to the presence of the saturated long chain fatty acids which are present. The most practical and the most preferred limits are about 1 to about 4% by weight of the margarine oil of saturated long chain arachidic and/or behenic acid with the ratio of short chain fatty acids containing 6 to 14 carbon atoms to these long chain fatty acids containing 20 to 22 carbon atoms being from 40:1 to 2:1. The long-chain arachidic and/or behenic acids should preferably be combined in a triglyceride molecule by corandomization with short chain fatty acids. Optimum benefits are achieved by maximizing the number of triglycerides which contain both long and short chain fatty acids and by minimizing the triarachidic and tribehenic triglycerides. The corandomized triglycerides which contain arachidic acid and/or behenic acid and 75 oil and from the milk slurry with an addition of 0.05 lb.

short chain fatty acids exhibit highly increased stiffening power and unique thixotropic characteristics which permit formulation of margarine with unusually low solid content at room temperature and good heat stability.

The long chain fatty acids containing 20 to 22 carbon atoms, arachidic acid and behenic acid, respectively, are desirably obtained by hydrogenation of rapeseed oil, mustard seed oil, wallflower seed oil, nasturtium seed oil, or marine oil. Rapeseed oil is the preferred source of the long chain fatty acids. The hydrogenation is carried out under the usual conditions of time, temperature and pressure conventional in the art in the presence of any suitable catalyst. Accordingly, details of the hydrogenation will not be given here. The hydrogenation must 15 be carried out until the oil has an iodine value (I.V.) of less than 30 and preferably less than 10, in order to achieve the advantages of the present invention.

Rapeseed oil or any of the other above-enumerated sources of long chain fatty acids which has been hydrogenated to an I.V. less than 30 should be used in an amount which is more than 0.6% by weight of the margarine oil but less than 25% by weight of the margarine oil. The greater the degree of hydrogenation, and hence the lower the I.V., the more acid in the oil will be converted to arachidic and/or behenic acid, and the less hydrogenated oil will be required to be corandomized with an oil containing short chain fatty acids to give the same effect.

The present invention improves the characteristics of 30 margarine prepared from margarine oils containing soybean oil, cottonseed oil, corn oil, sunflower oil, safflower seed oil, peanut oil and lard as well as those margarine oils in which tallow, palm oil, coconut oil, or palm kernel oil are used in amounts up to 40% by weight. If the tallow, palm oil, coconut oil or palm kernel oil is corandomized with an oil containing long chain fatty acids such as rapeseed oil, these oils can constitute up to about 60% by weight of the margarine oil. A corandomized blend such as this is simply mixed with an unhydrogenated or slightly hydrogenated soft oil; for example: 60% by weight soybean oil is blended with 40% by weight of a corandomized blend containing 12% by weight of the corandomized blend of highly hydrogenated rapeseed oil having an I.V. of about 4 and 88% by weight of the corandomized blend of palm kernel oil. In other margarine oil formulations the entire margarine oil is corandomized; for example: 38% by weight palm oil is corandomized with 12% by weight highly hydrogenated rapeseed oil having an I.V. of about 4 and 50% by weight coconut oil to give a good margarine oil. This corandomized margarine can be modified by the addition of any soft oil or mixtures thereof.

While it is not desired to limit the operation of the present invention to any particular theory, it is theorized 100:1 to 1:1. When the saturated long chain fatty acids 55 that the presence of the long chain fatty acids containing 20 to 22 carbon atoms provides the stiffening power which improves the heat stability of the margarine. The presence of the short chain fatty acids containing 6 to 14 carbon atoms on the same triglyceride molecule as the long chain fatty acids reduces the melting point of the triglyceride but still allows retention of the stiffening properties of the triglyceride at room temperature, thus providing an improved eating quality-heat stability balance.

The following examples are given to illustrate the present invention.

The margarines in the examples below were prepared by mixing the margarine oil with milk powder, salt and emulsifier in the following manner:

Eighty pounds of the margarine oil being tested was melted and heated to 110° F. in a hot water jacketed pilot plant mix tank. 1.65 pounds of commercial milk powder and 2 pounds of salt were mixed (slurried) in 15 pounds of water. An emulsion was prepared from the margarine

5

monoglycerides prepared from partially hydrogenated sovbean oil.

The margarine emulsion was chilled through a conventional Votator A unit assembly and a B unit. Votators (chillers) are well-known in the art, but a description of such apparatus may be found at pages 921–924 of A. E. Bailey, Industrial Oil and Fat Products, 2nd Ed., Interscience Publishers Inc., New York City, N.Y. (1951).

The extruded product was packed at approximately 40° F. and tempered as usual for 48 hours at 50° F.

#### Example 1

Forty parts of refined and bleached coconut oil were mixed with sixty parts of refined and bleached palm oil and the mixture corandomized.

A second blend was prepared which consisted of fifty parts refined and bleached coconut oil mixed with fifty parts refined and bleached highly hydrogenated rapeseed oil having an I.V. of about 4 and corandomized.

The corandomization was carried out under the following conditions: The oil mixtures were heated to 340° F. under a vacuum of about 10 mm. mercury and held under these conditions until dry. Catalyst was then added: this consisted of 0.22% glycerine plus 0.7% NaOH as 49% solution in water; but other catalysts such as sodium 2 methylate may be used. The reaction was carried out by maintaining the mixture at 340°-360° F. under about 10 mm. mercury vacuum until corandomization was complete, as indicated by samples taken and tested for SCI. Two successive samples showing closely agreeing SCI 3 values indicated completeness. After reacting as above, the mixture was cooled to 140° F. Throughout the entire heating, reacting, and cooling periods the mixture was agitated mechanically and a stream of nitrogen was passed through it. After cooling, the mixture was water-washed in an agitated kettle with about 4% of water, settled, decanted and then filtered.

The two blends were then mixed together with soybean oil which had been hydrogenated to an I.V. of about 95 in the proportions shown below, deodorized at 200° C. and a margarine prepared as described above. The margarines were tested by standard uniform testing procedures. Spreadability at 50° F. and eating quality were judged by a panel of experts and graded on a scale of 1 to 10, 1 being poor and 10 being excellent. Slump tests were also graded by a panel of experts on the same grading scale against standard photographs. Oil off figures were quantitatively determined by measuring the oil lost by a margarine sample after 48 hours at 85° F. The reported figures are the calculated percentages of lost oil.

	Control	Example 1
Coconut/palm corandomized blend (40 parts coconut oil and 60 parts palm oil), percent. Coconut/rapeseed corandomized blend (50 parts coconut oil and 50 parts rapeseed	88.5	75
oil), percentSoybean oil, percent	11.5	10 15
	100	100
Spreadability (50° F.) Oil-off 85° F./48 hours, percent Slump Eating quality (50° F.)	6. 5 24 2 7. 5	6. 5 1. 0 8 7. 1
SCI (80° F.): At 50° F. At 70° F. At 80° F. At 80° F.	30. 0 15. 9 9. 5 1. 9	32 17. 6 11. 8 3. 1

In Example 1, above, the proportion of short chain fatty acids having from 6 to 14 carbon atoms derived from a corandomized blend of coconut oil and palm oil garine oil while the proportion of long chain fatty acids having from 20 to 22 carbon atoms derived from the rapeseed oil was 1.8% by weight of the margarine oil. The ratio of short chain fatty acids (abbreviated SCFA) to long chain fatty acids (abbreviated LCFA) is 15.6:1.

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These results indicate that the margarine prepared from a corandomized blend of coconut oil and palm oil without the corandomized coconut oil and rapeseed oil additive gave a margarine which had a very good spreadability, poor oil-off and a very low grade in the slump test. On the other hand, when the additive of the present invention was added to the margarine oil and a margarine formed therefrom, there was no adverse effect on the excellent spreadability, a significant improvement on the slump, and a dramatic improvement in the oil-off quality.

#### Examples 2 and 3

Refined and bleached coconut oil was mixed with refined and bleached palm oil and refined and bleached highly hydrogenated rapeseed oil having an I.V. of about 4.0. The mixture was corandomized as before.

This mixture was blended with a small portion of refined and bleached soybean oil which was hydrogenated to an I.V. of about 95, then deodorized at 200° C. and a margarine prepared as previously described.

The proportions of the coconut oil, palm oil, rapeseed oil, and soybean oil are shown below as percent by weight.

25		Control	Example 2	Example 3
30	Coconut/palm corandomized blend, percent:     Coconut.     Palm. Coconut/palm/rapeseed corandomized blend, percent:     Coconut.     Palm. Rapeseed. Soybean oil, percent.	45 45 0 0 0 10.0	0 0 42. 5 42. 5 5. 0 10. 0	0 0 36.0 27.3 8.7 28.0
55	·	100	100	100

The margarines were tested in the standard manner as described in Example 1 and the results were as follows:

10		Control	Example 2	Example 3
<b>↓</b> 5	Spreadability Oil-off 85° F./48 hours, percent Slump Eating Quality (50° F.): SCI (80° F.): At 50° F At 70° F At 80° F At 92° F	5.8 25 2 7.8 33.8 16.7 9.9 1.1	5.8 2.2 6.8 7.8 34.9 17.9 10.6	8. 1 3. 6 6. 0 7. 5 29. 6 15. 3 9. 6 2. 4

In Example 2, the proportion of SCFA derived from the 42.5% by weight coconut oil is 34.2% by weight while the proportion of LCFA derived from the 5% by weight rapeseed oil is 1.8% by weight giving a ratio of SCFA to LCFA of 19:1. In Example 3, the proportion of SCFA derived from the 36.0% by weight coconut oil is 29% by weight while the proportion of LCFA derived from the 8.7% weight rapeseed oil is 3.1% by weight giving a ratio of SCFA to LCFA of 9.4:1. There are no significant quantities of long chain or short chain fatty acids in palm oil or soybean oil; therefore, the ratio of SCFA to LCFA is calculated by taking the short chain and long chain fatty acids in the coconut oil and rapeseed oil

These results also show, as in Example 1, that the addition of the additive of the present invention to a margarine oil gives a margarine in which there is no significant detrimental effect on the excellent spreadability, a significant improvement in the slump over a test margarine oil, and a dramatic improvement in the oil-off qualities.

### Example 4

For the control product refined and bleached soybean oil was hardened to an I.V. of about 81. Ninety parts of this were blended with 10 parts of refined and bleached 75 palm oil.

7

For the example product, refined and bleached soybean oil was hardened to an I.V. of about 107. Sixty-five parts of the refined and bleached soybean oil were blended with thirty-five parts of a corandomized blend consisting of 88% by weight of highly hydrogenated palm kernel oil having an I.V. of about 1.5 and 12% by weight of highly hydrogenated rapeseed oil having an I.V. of about 4. This corandomized blend was prepared as described in the previous examples.

The blended oils were deodorized and margarines made as described previously. The proportions of the various oils are shown below:

	Control	Example 4
Soybean oil (I.V. 81), percent Soybean oil (I.V. 107), percent Palm oil, percent Corandomized blend, percent: Palm kernel oil Rapeseed oil	0	0 65 0 30.8 4.2

The margarines were tested as described in Example 1 above, and the results are given below:

	Control	Example 4
Spreadability (50° F.)	7. 0	7.5
Spreadability (50° F.) Oil-off 85° F./48 hours, percent	4.2	1.0
Slump	5.5	8.0
Eating Quality (50° F.)	7.3	7.8
At 50° F	30, 4	28, 4
At 70° F	16.2	17.7
At 80° F	11.3	11.3
At 92° F	2.7	3. 2

In Example 4, the proportion of SCFA derived from the 30.8% by weight palm kernel oil is 23.6% by weight while the proportion of LCFA derived from the 4.2% by weight rapeseed oil is 1.4% by weight giving a ratio of SCFA to LCFA of 17:1.

These data also show the unusual effect on the oil-off of the additive of the present invention and illustrates that the eating quality may be improved without sacrificing the other beneficial qualities of the margarine.

What is claimed is:

1. A margarine oil adapted to be manufactured into a margarine of good spreadability, oil-off, slump and eating qualities comprising at least about 5% by weight of corandomized triglycerides containing saturated short

8

chain fatty acids having from 6 to 14 carbon atoms and saturated long chain fatty acids having from 20 to 22 carbon atoms, the amount of the saturated long-chain fatty acids being bout 0.3% to about 5.0% by weight of the margarine oil, the ratio of the saturated short chain fatty acids in the margarine oil to the saturated long chain fatty acids in the margarine oil being from 100:1 to 1:1.

2. The margarine oil of claim 1 wherein the balance of the portion of said margarine oil which is not corandomized triglycerides is an oil selected from the group consisting of soybean oil, cottonseed oil, corn oil, sunflower seed oil, safflower seed oil, peanut oil, lard and mixtures thereof.

3. The margarine oil of claim 1 wherein the saturated long chain fatty acids are selected from the group consisting of rapeseed oil, mustard seed oil, wallflower seed oil, nasturtium seed oil, marine oils and mixtures thereof, said oils being hydrogenated to an iodine value of less than 30.

4. The margarine oil of claim 1 wherein the short chain fatty acids are selected from the group consisting of palm kernel oil, coconut oil, and mixtures thereof.

5. A margarine oil adapted to be manufactured into 25 a margarine of good spreadability, oil-off, slump and eating qualities comprising at least about 5% by weight of corandomized triglycerides containing saturated short chain fatty acids having from 6 to 14 carbon atoms, said short chain fatty acids being selected from the group 30 consisting of palm kernel oil, coconut oil, and mixtures thereof, and saturated long chain fatty acids having from 20 to 22 carbon atoms, said saturated long chain fatty acids being hydrogenated to an iodine value of less than 10 and selected from the group consisting of rapeseed oil, mustard seed oil, wallflower seed oil, nasturtium seed oil, marine oils, and mixtures thereof, the amount of the saturated long chain fatty acids being about 1.0% to about 4.0% by weight of the margarine oil, the ratio of the saturated short chain fatty acids in the margarine oil 40 to the saturated long chain fatty acids in the margarine oil being 40:1 to 2:1.

## References Cited

# UNITED STATES PATENTS

3,298,837 1/1967 Seiden \_\_\_\_\_ 99—118

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