

1

3,592,661

**MARGARINE OILS CONTAINING INTERMEDIATE MELTING RANDOMLY ESTERIFIED TRIGLYCERIDES OF HIGH C<sub>12</sub> CONTENT****Paul Seiden, Cincinnati, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio****No Drawing. Filed Sept. 16, 1968, Ser. No. 760,061****Int. Cl. A23d 3/00****U.S. Cl. 99—122****4 Claims****ABSTRACT OF THE DISCLOSURE**

Margarine oils comprising a soft oil component and an intermediate melting, randomly esterified, triglyceride component of high C<sub>12</sub> content and low C<sub>16-18</sub> content exhibit improved solids content properties as shown by a bent and rapidly sloping SCI curve.

**BACKGROUND OF THE INVENTION**

The field of this invention is margarine oils. More specifically, the invention relates to margarine oils which have improved solids content properties.

Margarine consists of an emulsion of an oil or fatty phase and an aqueous phase. The physical characteristics of a finished margarine such as solids content properties, 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 in turn dependent on the percentages of the fatty matter which exist in the solid state at the various temperatures normally encountered during the 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 the margarine 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 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 appearance 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. This is particularly true of the newer type so-called soft margarines which are packaged in tub form.

When some margarines are heated above about 70° F., part of their liquid oil content may start to seep or "oil-off" 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, soiling the container. 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.

The conventional way of improving heat resistance of a margarine is to increase the higher melting saturated

2

or trans fatty acid glyceride content by further hardening of 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. Conversely, past attempts to modify the solids content properties of margarine have often resulted in loss of heat stability. This discussion is applicable to either stick-type or tub-type margarines.

The solids content referred to hereinabove is expressed at different temperatures in terms of a "Solids Content 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, pp. 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. Thus a "bent" SCI curve and particularly one that is rapidly sloping between 80° F. and 86° F. is a highly desired goal in the formulation of margarine oils. Achievement of these solids content properties without sacrifice of other properties such as spreadability, eating quality and stability is especially desirable. The following references provide further background in the field of the invention: U.S. Pat. 3,006,771, U.S. Pat. 2,921,855, U.S. Pat. 3,353,964, U.S. Pat. 3,494,944.

**SUMMARY OF THE INVENTION**

The margarine oils of the present invention have a normal solids content at cool or refrigeration temperatures, e.g., 50° F., a normal solids content at room temperature, e.g., 70° F. or 80° F., and a very low solids content at mouth temperatures, e.g., 92° F. The SCI curve exhibited by these margarine oils is, therefore, highly bent in the desired manner. Moreover, and more importantly, the SCI curve exhibits a sharp or rapid slope in the area of 80°-86° F. Translating this SCI data into terms of eating quality and physical properties, margarine can be provided which has a highly improved eating quality (due to the low solids content at 92° F.), a superior melt in the mouth characteristic (due to the rapid change in solids content between 80°-86° F. as shown by the sharp slope of the SCI curve in this area), and adequate heat stability and spreadability (due to the normal solids content at 70°-80° F.), and improved storage stability (due partially to the solids content at cool temperatures and the polymorphic phase structure).

Margarine oils having the above-described properties are obtained, in accordance with the present invention, by the combination of a soft margarine oil component with a novel intermediate melting randomly esterified triglyceride component having a fatty acid content of 87%-97% C<sub>12</sub> and 3%-13% C<sub>16-18</sub>. In greater detail, the invention provides margarine oil having an SCI slope between 80° F. and 86° F. of at least 0.7, said slope being from about 3 to about 7 times greater than the SCI slope between 50° F. and 70° F., which comprises

- (a) from about 60% to about 80% soft margarine base oil, and  
 (b) from about 20% to about 40% randomly esterified triglyceride having a fatty acid composition comprising from about 87% to about 97% saturated  $C_{12}$  and from about 3% to about 13% saturated  $C_{16-18}$ .

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The soft oil component of the margarine oils of this invention can be any normally liquid glyceride oil or oil fraction. Suitable soft oil glycerides can be derived from animal, vegetable, or marine sources, including naturally occurring triglyceride oils and fats such as cottonseed oil, soybean oil, peanut oil, rapeseed oil, palm oil, corn oil, crambe oil, sunflower seed oil, safflower seed oil, lard tallow, marine oils, and the like. The preferred soft oil component is selected from cottonseed oil, corn oil, safflower seed oil, rapeseed oil, sunflower seed oil, palm oil, soybean oil (the soybean oil preferably being hydrogenated in an I.V. of from about 90 to about 125) and mixtures thereof.

Natural soybean oil has an iodine value (I.V.) which varies between about 110 and about 150 with an average being about 130. Soybean oil is preferably partially hydrogenated to prevent flavor deterioration caused by the more highly unsaturated components such as the glycerides of linolenic acid. The partial hydrogenation of soybean oil can be accomplished by any one of a number of well known techniques, all of which involve contacting the oil with gaseous hydrogenation in the presence of a catalyst such as nickel and/or copper. See, for example, U.S. Pat. 2,168,603.

It is desirable that soft oil component, e.g., cottonseed oil or partially hydrogenated soybean oil, be refined and bleached in accord with conventional practice. See, for example, Bailey's Industrial Oil & Fat Products, 3rd ed., pp. 719 et seq.

The intermediate melting triglyceride component in the margarine oils of this invention must be randomly esterified and have a fatty acid composition comprising from about 87% to 97% saturated  $C_{12}$  (lauric acid) and from about 3% to about 13% saturated  $C_{16-18}$  (palmitic acid, stearic acid and mixtures thereof). Since technical grades of lauric, palmitic, and stearic acid are often conveniently used, the fatty acid composition of this triglyceride component can contain up to about 6% total of myristic, caprylic and capric acid. The intermediate melting triglyceride component is preferably substantially free from  $C_{20}$  or higher fatty acids. A preferred fatty acid composition comprises from about 90% to about 97% saturated  $C_{12}$  and from about 3% to about 10% saturated  $C_{16}$ .

Random esterification of the intermediate melting triglyceride with the specified fatty acids is an essential part of this invention. It has been discovered that mere physical blends, e.g., of 94% trilaurin and 6% tripalmitin, do not provide margarine oils having the desired bent SCI curve, and especially an SCI curve with a sharp slope between 80° F. and 86° F. The margarine oil can, of course, contain other triglycerides in physical combination with the required randomly esterified triglyceride. Also, two separate randomly esterified intermediate melting triglyceride components can be used in physical combination.

The intermediate melting triglyceride component can be readily prepared by conventional random transesterification, interesterification or rearrangement reactions between, for example, trilaurin and tripalmitin, or trilaurin and palmitic acid. See, Bailey's, pp. 946-965. A suitable method for preparing a random triglyceride of proper fatty acid content is to interesterify trilaurin with tripalmitin and/or tristearin according to the process of Burgers et al. as disclosed in U.S. Pat. 3,170,798, Feb. 23, 1965. A very desirable material for use as the intermediate melting triglyceride component herein is commercially avail-

able technical grade trilaurin which is randomly esterified and has a fatty acid composition of about 95.4%  $C_{12}$ , 3.4%  $C_{16}$ , and 1%  $C_{10}$ .

The margarine oils of the invention comprise from about 60% to about 80% of the soft oil component and from about 20% to about 40% of the intermediate melting triglyceride component. Preferred margarine oils comprise from about 70% to about 78% of the soft oil component and from about 22% to about 30% of the randomly esterified triglyceride component. The two components of the margarine oil are preferably present together in a physical blend; chemical reaction such as interesterification is not necessary or desirable. The exact proportion of soft oil and other components can be varied depending upon whether a stick-type or a soft-type margarine is desired.

The margarine oils defined above have highly desirable solid content properties. These oils have a normal solids content at cool or refrigeration temperatures, e.g. 50° F., a normal solids content at room temperature, e.g., 70° F. or 80° F., and a very low solids content at mouth temperatures, e.g., 92° F. The SCI curve exhibited by these margarine oils is, therefore, bent in the desired manner. Moreover, and more importantly, the SCI curve exhibits a sharp or rapid slope in the area of 80°-86° F. Translating this SCI data into terms of eating quality and physical properties, margarine can be provided which has a highly improved eating quality (due to the low solids content at 92° F.), a superior melt in the mouth characteristic (due to the rapid change in solids content between 80°-86° F. as shown by the sharp slope of the SCI curve in this area), an adequate heat stability and spreadability (due to the normal solids content at 50° and 70°-80° F.), and improved storage stability (due partially to solids content at cool temperatures and the polymorphic phase structure).

In more detail, the margarine oils of the invention can have an SCI of from about 12 to about 30, preferably from about 15 to about 25, at 50° F.; an SCI of from about 5 to about 25, preferably from about 10 to about 20, at 70° F.; an SCI of from about 5 to about 15, preferably from about 5 to about 12, at 80° F.; an SCI of from about 0 to about 7, preferably from about 1 to 3, at 86° F.; and an SCI of less than about 2, preferably about 0, at 92° F. Most significantly, the SCI curve for the margarine oils is sufficiently bent so that it slopes at least about 0.7, preferably from about 0.8 to about 3.0, SCI units per degree F. between 80° F. and 86° F. and this 80°-86° F. slope is from about 3 to about 7 times, preferably from about 4 to about 6 times, greater than the SCI slope between 50° F. and 70° F.

Although margarine oils have been prepared in the past that have one or more of the desired solids content properties described above for the margarine oils of this invention, none have exhibited the overall SCI curve of the present margarine oils. Particularly significant is the rapidly sloping nature of the curve between 80° F.-86° F. which provides a superior melt in the mouth eating quality and the bent nature of the curve to maintain a proper solids content at lower temperatures. In addition, the present margarine oils exhibit an unexpectedly high degree of storage stability, i.e., they retain their superior eating qualities after long periods of storage or temperature cycling, for example, at 80° F. or 85° F. for up to 24 hours.

The margarine oils of the present invention are further unique in that they appear to convert rapidly and permanently into the beta crystalline phase during conventional processing and tempering of the margarine. Conventional margarines are normally in the beta-prime crystalline phases. These phases are described and defined by Mitchell in U.S. Patent 2,521,241, Sept. 5, 1950. The exceptional storage stability of the present margarine oils is believed attributable to their beta phase crystalline form as well as to their solids content properties.

## 5

Margarines of conventional formulation can be prepared by the usual processes from the margarine oils of the present invention. See Bailey's, supra page 331 et seq. or the United States Federal Standards of Identity for Margarine. Preferably, the margarines contain from about 70% to about 90% of the margarine oil, from about 1% to about 3% milk solids nonfat, and from about 10% to about 30% water.

## Example I

(a) Intermediate melting randomly esterified triglyceride component.—A mixture of 92% trilaurin and 8% tripalmitin was charged to a stainless steel deodorizer equipped with a refluxing condenser. Refluxing, with agitation by nitrogen sparging, for 2 hours at 500 mm. Hg and 255° C. produced a randomly esterified intermediate melting triglyceride having a fatty acid composition of 92% lauric and 8% palmitic. The esterification was followed with conventional deodorization at 5 mm. Hg absolute pressure and 220° C.

Commercially available technical grade trilaurin was used as a second intermediate melting randomly esterified triglyceride. This material had a fatty acid composition of 95.4% C<sub>12</sub>, 3.4% C<sub>16</sub>, and 1% C<sub>10</sub>.

(b) Margarine oil.—The triglycerides of step (a) were blended with refined and deodorized bleached cottonseed oil, rapeseed oil and soybean oil to form a margarine oil of the following composition:

Component:	Percent by weight
Intermediate melting randomly esterified triglyceride (92% C <sub>12</sub> , 8% C <sub>16</sub> )	13
Intermediate melting randomly esterified triglyceride (95.9% C <sub>12</sub> , 3.4% C <sub>1</sub> , 1% C <sub>10</sub> )	16
	29
Cottonseed oil	20
Rapeseed oil	11
Soybean oil	40
	71
	100

(c) Margarine.—The margarine of this example is suitable for packaging in "stick" form and was prepared by mixing the margarine oil with milk powder, salt and emulsifier in the following manner:

Eighty pounds of the margarine oil was melted and heated to 110° F. in a hot water-jacketed 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 oil and from the milk slurry with an addition of 0.05 lb. monoglycerides prepared from partially hydrogenated soybean 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 and a description of such apparatus can be found in Bailey's, supra.

The extruded product was packed at approximately 40° F. and tempered as usual for 48 hours at 50° F. The triglyceride solids appeared to be in the beta crystalline phase. The margarine was 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 80° F. The reported figures are the calculated percentages of lost oil.

## 6

Spreadability (40° F.)	6.5
Oil-off 80° F./24 hours, percent	None
Slump 80° F./24 hours	10
Eating quality (40° F./60° F.)	8.5/9.0
SCI (80° F.):	
At 50° F.	22.5
At 70° F.	17.8
At 80° F.	11.2
At 86° F.	4.8
At 92° F.	0.0

The indicated data provided the SCI curve for the above margarine. It can be observed from the data that the curve is bent in the desirable manner and is rapidly sloping between 80° F. and 86° F. The slope of the SCI curve between 80°–86° F. is 1.07 (6.4 SCI units per 6 degrees F.) which is 4.5 times greater than the 0.235 slope of the SCI curve between 50° F.–70° F. (4.7 SCI units per 20 degrees F.).

## Example II

(a) Intermediate melting randomly esterified triglyceride component.—A mixture of 96% trilaurin and 4% tripalmitin was reacted as in Example I to produce an intermediate melting randomly esterified triglyceride having a fatty acid composition of 96% lauric and 4% palmitic.

(b) Margarine oil.—The triglyceride of step (a) was blended with an 80:20 mixture of trilaurin and tricaprln, cottonseed oil, partially hydrogenated soybean oil (I.V. 107), and rapeseed oil, to form a margarine oil of the following composition:

Component:	Percent by weight
Intermediate melting randomly esterified triglyceride (96% C <sub>12</sub> , 4% C <sub>16</sub> )	22
Randomly esterified mixture of trilaurin and tricaprln (80% C <sub>12</sub> , 20% C <sub>10</sub> )	6
Cottonseed oil	20
Soybean oil (I.V. 107)	50
Rapeseed oil	2
	72
	100

(c) Margarine.—Margarine, suitable for packaging in "stick" form, was prepared from the above margarine oil as in Example I with the evaluation data shown below.

Spreadability (50° F.)	7.8
Oil-off 80° F./24 hours, percent	None
Slump 80° F./24 hours	7
Eating quality 40° F./60° F.	7.3/9.0
SCI (80° F.):	
At 50° F.	16.9
At 70° F.	12.7
At 80° F.	8.4
At 86° F.	2.0
At 92° F.	0.0

The indicated data provide the SCI curve for the above margarine. It can be observed from the data that the curve is bent in the desirable manner and is rapidly sloping between 80° F. and 86° F. The slope of the SCI curve between 80°–86° F. is 0.95 which is 4.3 times greater than the 0.21 slope of the SCI curve between 50°–70° F.

## Example III

A soft-type margarine suitable for packaging in "tub" form was prepared by blending 23% of the intermediate melting randomly esterified triglyceride of Example II (96% C<sub>12</sub>, 4% C<sub>16</sub>) with 77% safflowerseed oil, the margarine was processed as in Example I except it was passed through a picker box mixer instead of the Votator B unit and packed into tubs. Evaluation data for the margarine are shown below.

Spreadability (40° F.) -----	8.3
Eating quality 40° F./60° F. -----	8.5/8.5
SCI (80° F.):	
At 50° F. -----	15.5
At 70° F. -----	11.7
At 80° F. -----	7.0
At 86° F. -----	1.3
At 92° F. -----	0.0

The indicated data provide the SCI curve for the above margarine, Curve III in the drawing. It can be observed from the data that the curve is bent in the desirable manner and is rapidly sloping between 80° F. and 86° F. The slope of the SCI curve between 80°-86° F. is 0.95 which is 5 times greater than the 0.19 slot of the SCI curve between 50°-70° F.

In this example, substantially equivalent margarine is obtained in terms of a bent and rapidly sloping SCI curve when the palmitic acid of the random intermediate melting triglyceride is replaced by stearic acid and/or the safflowerseed oil is replaced by corn oil, palm oil, or sunflower seed oil.

For comparative purposes, conventional butter, a commercially available typical stick margarine (75% partially hardened soybean oil, 25% corn oil), and a commercially available typical soft margarine (88% partially hardened soybean oil, 12% partially hardened palm oil) were obtained and evaluated for solids content and other properties; these data are shown below.

	Butter	Stick margarine	Soft margarine
Spreadability, 40° F./60° F. -----	4.0/8.0	7.0/8.0	8.7/—
Eating quality, 40° F./70° F. -----	7.5/8.4	7.0/7.5	6.0/6.9
Oil-off 80° F., 24 hours -----		None	
Slump -----		10	5
SCI (80° F.):			
At 50° F. -----	28.3	25.8	13.1
At 70° F. -----	11.5	14.3	8.3
At 80° F. -----	8.2	9.7	6.3
At 86° F. -----	6.4	7.0	4.8
At 92° F. -----	3.2	3.3	2.8

The indicated data provide the SCI curves for the above products. A comparison of these curves with SCI curves

for the invention margarine of Examples I, II, and III shows how unique and desirable solids content properties have been achieved with margarines based on the margarine oils of the present invention.

I claim:

1. Margarine oil having an SCI slope between 80° F. and 86° F. of at least 0.7, said slope being from about 3 to 7 times greater than the SCI slope between 50° F. and 70° F., which consists essentially of

(a) from about 60% to about 89% soft margarine base oil, and

(b) from about 20% to about 40% randomly esterified triglyceride having a fatty acid, composition consisting essentially of from about 87% to about 97% saturated C<sub>12</sub> and from about 3% to about 13% saturated C<sub>16-18</sub>; and not containing more than about 6% total of myristic, caprylic, and capric acid; and which is substantially free of C<sub>20</sub> or higher fatty acids.

2. The margarine oil of claim 1 wherein the base oil is selected from the group consisting of cottonseed oil, corn oil, safflower seed oil, rapeseed oil, sunflower seed oil, palm oil, soybean oil, and mixtures thereof.

3. The margarine oil of claim 2 wherein the randomly esterified triglyceride fatty acid composition consists essentially of from about 90% to about 97% saturated C<sub>12</sub> and from about 3% to about 10% saturated C<sub>16</sub>.

4. The margarine oil of claim 3 which consists essentially of from about 70% to about 78% of the base oil and from about 22% to about 30% of the randomly in units per 20 degrees F.).

# References Cited

## UNITED STATES PATENTS

2,442,535	6/1948	Eckey	99—118X
3,494,944	2/1970	Seiden	99—118X

JOSEPH M. GOLIAN, Primary Examiner

U.S. Cl. X.R.

99—118

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,592,661

Dated July 13, 1971

Inventor(s) Paul Seiden

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- At column 3, line 16, a comma should be inserted after "lard"
- At column 4, line 18, "scontent" should read -- content --
- At column 5, line 35, " $C_1$ ," should read --  $C_{16}$  --
- At column 6, lines 35 and 70, "randamly" should read  
-- randomly --
- At column 7, line 32, "6.0/6.9" should read -- 6.0/6.5 --
- At column 7, line 34, "5" should read -- 9 --
- At column 8, line 10, "89%" should read -- 80% --
- At column 8, line 31, delete "in units per 20 degrees F.)."  
and insert -- esterified triglyceride. --
- Signed and sealed this 25th day of January 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents