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(54) **Method for interesterifying an edible oil.**

(57) A method for treating an edible oil rich in linoleic acids so as to increase its solid fat content comprises the directed interesterification under isothermal conditions of an oil containing at least 60% pufa and 12.5 to 16% safa, with preferably at least a part of the safa being hydrogenated, having been cooled to its interesterification temperature at a cooling rate of between 5°C/min and 5°C/s. The method is simple to perform and produces an oil which can be employed directly in margarine manufacture. The oil can be a mixture of an oil high in pufa such as natural sunflower and safflower seed oil and an oil high in safa such as fully or partially hardened sunflower or safflower seed oil. The initial rapid cooling rate can increase the rate of development of solid fat phase during the interesterification step.

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METHOD FOR TREATING AN EDIBLE OIL

The present invention relates to a method for treating an edible oil, to an oil so prepared and to margarine produced from the said oil.

An oil suitable for use in margarine manufacture is conventionally prepared from a mixture of triglycerides obtained from a vegetable, animal and/or a marine source by full or partial hydrogenation of any unsaturated fatty acids present. Other methods of raising the melting point of a triglyceride mixture and, hence, its solid phase content at ambient temperature are, however, known. One of these methods is so-called directed interesterification of the triglyceride mixture and is for example described, mainly in relation to plastic shortenings, by Eckey in his US Patent Specification No. 2,442,532. In essence, the method comprises the addition of a catalyst to the oil mixture to cause random redistribution of the fatty acids, followed by cooling to a temperature at which at least one of the triglycerides present crystallises out of solution. The said triglyceride or triglycerides formed by the random action of the catalyst and crystallising out of solution cause the statistical distribution of the interesterification products formed to be upset. Further high melting triglyceride is thus preferentially formed in

an attempt to restore the equilibrium and continues to crystallise.. Once sufficient of the solid triglyceride has formed to bring the mixture to an overall desired solid phase content the reaction is stopped. Various elaborations to the basic concept are described in the US specification. The all-liquid triglyceride mixture can, for example prior to interesterification, be first slightly cooled to crystallise some of the high melting triglyceride which subsequently acts as seed crystals.

In recent years a demand has existed for margarine oils which are high in polyunsaturated fatty acids (pufa). To retain an overall high degree of unsaturation and yet increase the solid phase content of the oil, the use of directed interesterification in a variety of modified forms has been suggested for margarine oils high in pufa. These various modifications are intended to accelerate the basic process which is described in US Specification No. 2,442,532 and which can, in some instances, take several days to perform.

UK Patent Specification No. 1,381,721 describes a process for directed interesterification of glyceride esters in which the mixture is alternately subjected, at least three times, to a temperature below the cloud point of a randomised mixture of the triglycerides, followed by a temperature above the cloud point of the mixture. The specification asserts that suitable margarine oil can be prepared from, for example, sunflower oil, after only 24 hours of so-called temperature cycling. European Patent Application No. 79 103419 (Publication No. 0,009,207) describes another directed interesterification process suitable for oils high in pufa in which temperature cycling occurs in a number of closely specified heating and cooling steps.

Although successful in increasing the solid fat content of pufa oils in a relatively short period, the processes described in UK Specification No. 1,381,721 and European Specification No. 9,207 each requires close monitoring and control of the temperature of the mixture with a consequent increase in manufacturing costs and equipment.

In our pending patent application European Patent Application No. 82 301200 we described a method for treating a triglyceride oil in which the reaction rates attained, as measured by increase in solid fat content, are comparable to those obtained employing temperature cycling techniques. The method described in EP 82 301200 comprises subjecting an oil rich in pufa and having a certain safa (saturated fatty acid) content to directed interesterification under isothermal conditions. The absence of temperature cycling requirements obviates the need for a succession of closely monitored and controlled different steps and thus leads to a cost reduction.

We have now discovered an improvement to the method described in EP 82 301200 which can retain the cost advantages of the isothermal method and yet can lead to a decrease in the time required to achieve a certain solid fat content in the oil.

According to the present invention there is provided a method for treating an edible oil having triglycerides rich in linoleic acid characterised in that the oil has a pufa (polyunsaturated fatty acid) content of at least 60% and a safa (saturated fatty acid) content of between 12.5% and 16%, the method comprising bringing the oil into contact with an interesterification catalyst, cooling the reaction mixture at a cooling rate within the range of from about 5°C per minute to about 5°C per second to a

temperature at which directed interesterification will occur and maintaining the reaction mixture under isothermal conditions at said temperature.

It is to be understood that the present invention extends to oils treated by the present process and to margarine prepared from the said oils. Throughout the present specification all percentages are by weight and the terms "oil" and "fat" are used interchangeably. By "isothermal conditions" we mean a temperature which is maintained substantially constant. Slight fluctuations may occur without deviating from the present invention. The term "fatty acids" is taken to mean fatty acid moieties forming part of the triglycerides.

The reaction mixture is preferably cooled at the present cooling rate from a temperature at which the interesterification catalyst is activated. The activation temperature suitably lies within the range of from 45°C to 75°C. Where an activation temperature in the region of 70°C is selected the temperature need only be maintained momentarily. Where however an activation temperature is selected in the region of 50°C the reaction mixture is preferably maintained at this temperature for a few minutes before cooling commences. Suitable catalysts for use in the present process include sodium ethoxide, potassium ethoxide, sodium methoxide, potassium methoxide and sodium/potassium alloys. The controlled cooling step can for example be performed by employing a heat exchanger such as a plate heat exchanger.

The edible oil used in the present process may consist of one or more naturally occurring oils. Preferable however at least a part of the safa content of the oil comprises hydrogenated fatty acids. Suitably the hydrogenated fatty acids comprise 3 to 5% of the edible

oil subjected to the present process. The pufa content of the edible oil is preferably provided in total by linoleic acid.

Preferably all oils have, if necessary, been refined prior to the present process to remove for example any free fatty acids present. Suitably the edible oil can comprise a blend of oils comprising one or more, preferably naturally occurring, oils having a high pufa content and one or more oils having a high safa content. By "high" we mean at least 35wt%, preferably at least 50 wt%, more preferably at least 70 wt%. The oil having a high safa content can for example be a fully or partially hydrogenated oil and may be a fully or partially hydrogenated sample of the oil having a high pufa content. It may alternatively comprise a hydrogenated fat randomly interesterified with another fat. In a preferred embodiment of the present process an oil having a high pufa content is mixed with an oil high in safa to produce a blend of oils having the required fatty acid composition. Suitably the blend of oils comprises from 95 to 97% naturally occurring oil having a high pufa content and 5 to 3% oil having a high safa content. The process can and preferably is performed in the absence of any solvent.

Examples of oils having a high pufa content which have been found to be particularly suitable for use in the present process include sunflower oil and safflower seed oil. A suitable temperature for performing the directed interesterification step with both sunflower oil and safflower seed oil has been found to lie in the range of from about -5°C to about 12°C, preferably from about 0°C to 8°C and is most preferably about 3°C at which temperature the triglycerides crystallising out of solution comprise substantially a mixture of trisaturated glycerides and mono unsaturated triglycerides.

By means of the present process it is possible to produce an oil which can be employed in the manufacture of margarine as the sole fatty ingredient in the fatty phase, the oil having a ratio of polyunsaturated fatty acids to saturated fatty acids (p/s ratio) of at least 3.75. Preferably, however, the fat blends are selected within the limits of the present invention to achieve a p/s ratio of at least 4 and more preferably of at least 4.5. Preferably, the blend of oils contains at least 65% pufa and between 12.5 and 15% safa.

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawing which illustrates in graph form the increase in solid content of reaction mixtures as interesterification proceeds.

Example 1

A blend of 4.5 wt% sunflower seed oil hardened to a melting point of 69°C and 95.5 wt% safflower seed oil, the blend having a pufa content of about 73wt% and a safa content of about 14 wt%, was heated in a closed vessel to 50°C. 0.6% by weight with respect to the oil blend of dry NaOEt was sucked into the vessel and the temperature held briefly at 50°C to activate the catalyst. The mixture of oil and catalyst was passed through a plate heat exchanger at a controlled rate of cooling to attain a temperature of 3°C. The mixture was then retained at 3°C for at least 24 hours. Samples were taken periodically from the reaction mixture and assessed for their solid fat content at 3°C. N_{20} values of the same samples were assessed after destruction of the catalyst. Interesterification reaction was stopped by addition of water.

Two separate experiments were performed according to the above procedure. In one experiment the rate of

cooling in the plate heat exchanger was 0.5°C/sec and in a comparative experiment the rate of cooling was 10^{-3}°C/sec. The results are illustrated graphically in the figure. The two full lines in the figure represent the solid fat content when measured at 3°C and 20°C respectively as a function of interesterification time of a reaction mixture cooled at a rate of 0.5°C/s and interesterified isothermally at a temperature of 3°C. The dashed lines represent the same variables also as a function of interesterification time of a reaction mixture subjected to a cooling rate to 3°C of 10^{-3}°C/s.

The more rapid increase in solid fat content as the interesterification reaction proceeds is clearly shown for the mixture of oil and activated catalyst subjected to the faster cooling rate.

To provide an oil suitable for use in margarine manufacture in the absence of further added hard fat, the interesterified oil should exhibit an N_{20} value of at least 4, preferably at least 5. The interesterified oil subjected to an initial cooling rate of 0.5°C/s reaches an N_{20} value of 5 within 24 hours or less. Interesterification of the comparative reaction mixture for a total time of 60 hours was necessary to achieve a N_{20} value of 5.

Example 2

Experiments were performed on two separate 100 kg batches of an oil blend comprising 4.5 wt% sunflower seed oil hardened to a melting point of 69°C and 95.5 wt% safflower seed oil and having a pufa content of about 73wt% and safa content of about 14 wt%. In each case the batch of oil was heated to 70°C, 0.8wt% with respect to the oil of NaOEt was sucked in and the resulting mixture immediately thereafter subjected to cooling at a

predetermined cooling rate until a temperature of 3°C was reached. Each mixture was retained at 3°C for 10 hours at the end of which time the interesterification reaction was stopped and the solid fat content of each batch was measured at 10°C, 20°C, 30°C and 35°C respectively in terms of N values. In one experiment the cooling rate was arranged to be 0.5°C/min and in another experiment 5°C/min. The results in terms of the N values are given in Table I below.

TABLE I

Cooling rate	N_{10}	N_{20}	N_{30}	N_{35}
0.5°C/min	3.2	1.9	0.5	0.3
5.0°C/min	6.6	3.6	2.1	1.1

The greater development of solid fat content can be seen in the case of the experiment having the faster cooling rate.

Example 3

Experiments were performed to compare the interesterification time required to achieve certain N values of a reaction mixture held at a substantially fixed temperature and reaction mixtures subjected to temperature cycling. In each case the materials and procedure described in Example 1 were followed, each reaction mixture being cooled from an activation temperature of 50°C at a rate of 0.5°C/s. Of the four experiments performed one maintained a substantially constant interesterification temperature of 3°C for 24 hours whilst in the other three experiments the temperature was cycled six times over a two hour cycle and then held constant at 3°C for a further 12 hours. Each cycle consisted of a 30 minute period at a

set low temperature, a 30 minute period during which the temperature continually increased to a set high temperature, a 30 minute period at the set high temperature and a 30 minute cooling period to return to the set low temperature.

The results in terms of N_{10}, N_{20} and N_{35} after 24 hours interesterification are given in Table II below. The "high" and "low" refer to the set high and low temperatures employed in the temperature cycling routines. The last entry is the isothermal directed interesterification experiment. The results indicate that isothermal directed interesterification in combination with rapid cooling yield as good if not better results than those obtained with complicated temperature cycling routines.

TABLE II

Low T(°C)	High T(°C)	N_{10}	N_{20}	N_{35}
-5	+10	8.2	5.7	2.3
-5	+3	8.4	5.7	2.0
+6	+15	6.8	5.3	2.3
+3	+3	9.1	5.7	2.6

Example 4

Employing an oil blend of 4.5 wt% sunflower oil hardened to a melting point of 69°C and 95.5 wt% safflower seed oil, as in Example 1, together with 0.8 wt% NaOEt the effect of different temperatures for the isothermal directed interesterification was investigated. In each case the procedure of Example 1 was followed, employing a cooling rate of 0.5°C/s.

The results in terms of N_{10}, N_{20} and N_{35} values after 24 and 72 hours interesterification respectively are given in Table III below.

TABLE III

Interesterification temperature (°C)	N_{10} (after 24 hours)	N_{20} (after 24 hours)	N_{35} (after 24 hours)	N_{10} (after 72 hours)	N_{20} (after 72 hours)	N_{35} (after 72 hours)
-3	8.7	2.8	0	9.2	4.1	0.2
+3	9.1	5.7	2.6	10.2	7.0	2.6
+8	7.4	5.3	2.1	9.2	7.0	3.0

For the present oil blend and temperatures investigated the most efficient interesterification temperature in terms of rate of increase in SFC with reaction time is +3°C.

Each of the oils prepared in Examples 1, 3 and 4 embodying the present invention were suitable for use in manufacture of margarine according to conventional practice. The present oils are preferably used in manufacture of margarine as soon as possible after their treatment.

CLAIMS:

1. Method for treating an edible oil having triglycerides rich in linoleic acid characterised in that the oil has a pufa (polyunsaturated fatty acid) content of at least 60% and a safa (saturated fatty acid) content of between 12.5% and 16%, the method comprising bringing the oil into contact with an interesterification catalyst, cooling the reaction mixture at a cooling rate within the range of from about 5°C per minute to about 5°C per second to a temperature at which directed interesterification will occur and maintaining the reaction mixture under isothermal conditions at said temperature.

2. Method according to Claim 1 wherein the reaction mixture is cooled at the said cooling rate from a temperature at which the interesterification catalyst in contact with the oil is activated.

3. Method according to Claim 2 wherein the temperature at which the interesterification catalyst is activated lies within the range of from about 45°C to about 75°C.

4. Method according to any one of the preceding claims wherein the oil is directed interesterified at a temperature within the range of from about -5°C to about 12°C.

5. Method according to Claim 4 wherein the oil is directed interesterified at a temperature within the range of from about 0°C to about 8°C.

6. Method according to any one of the preceding claims wherein the oil is subjected to directed interesterification for less than 24 hours.

7. Method according to any one of the preceding claims wherein the oil has a pufa content of at least 65%.

8. Method according to any one of the preceding claims wherein the oil has a safa content of between 12.5% and 15%.

9. Method according to any one of the preceding claims wherein at least a part of the safa content of the oil comprises hydrogenated fatty acids.

10. Method according to any one of the preceding claims wherein the oil comprises a blend of at least one oil having a high pufa content and at least one oil having a high safa content.

11. Method according to Claim 10 wherein the oil having a high safa content comprises a fully or partially hydrogenated oil.

12. Method according to Claim 10 or Claim 11 wherein the oil having a high safa content comprises a fully or partially hydrogenated oil randomly interesterified with another oil.

13. Method according to Claim 11 or Claim 12 wherein the said fully or partially hydrogenated oil comprises fully or partially hydrogenated sunflower oil and/or safflower seed oil.

14. Method according to any one of Claims 10 to 11 wherein the oil having a high pufa content is selected from sunflower oil, safflower seed oil and a mixture thereof.

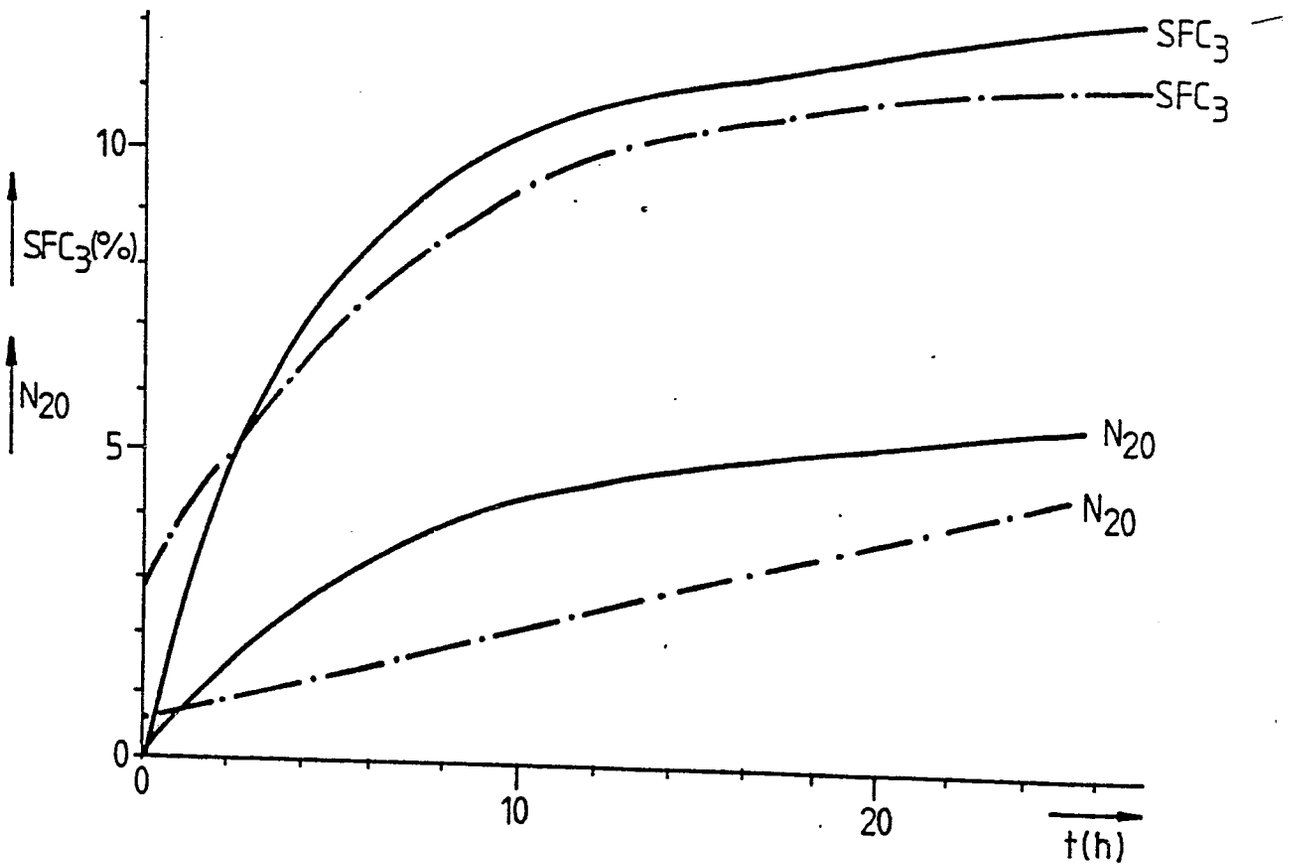
15. Method according to any one of Claims 10 to 14 wherein the oil comprises 95 to 97% oil having a high pufa

content and 5 to 3% oil having a high safa content.

16. Method according to any one of the preceding claims wherein the oil is a margarine oil.

17. Oil prepared by a method according to any one of the preceding claims having a pufa:safa ratio of at least 3.75.

18. Margarine containing an oil according to Claim 17.


SFC3
SFC3
10
SFC3(%)
N20
5
N20
N20
0
0
10
20
t(h)