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(21) International Application Number: PCT/DK91/00017 (22) International Filing Date: 22 January 1991 (22.01.91) (30) Priority data: 0169/90 22 January 1990 (22.01.90) DK (71)(72) Applicants and Inventors: KATBORG, Jon [DK/DK]; Lien 15, Vester Vandet, DK-7700 Thisted (DK). POUL- SEN, Kent, Elgaard [DK/DK]; Tystrupvej 47, DK-4250 Fuglebjerg (DK). (74) Agent: LEHMANN & REE; Frederiksberg Allé 26, DK- 1820 Frederiksberg C (DK).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (Euro- pean patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i>
(54) Title: A NON-LIQUID FATTY PRODUCT CONTAINING WATER AND AT LEAST ONE POLYUNSATURATED FATTY ACID AND A PROCESS FOR THE PRODUCTION OF SAME		
(57) Abstract A non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant and a process for the production of same wherein an inert gas is whipped into an emulsion wherein the oil phase is initially softened by heating which oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds and wherein the emulsion contains at least 1 percent by weight of oxygen-deficient water. Thus, protection of the fatty product against oxidation is accomplished and at the same time a suitable texture is imparted thereto.		

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A NON-LIQUID FATTY PRODUCT CONTAINING WATER AND AT LEAST ONE POLYUNSATURATED FATTY ACID AND A PROCESS FOR THE PRODUCTION OF SAME.

BACKGROUND OF THE INVENTION.

5 The present invention relates to a non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water, and optionally an antioxidant.

10 In a known process (Gillies, M.T., Shortenings, Margarines and Food Oils, Noyes Data Corporation, New Jersey, 1974, 333 pp.) for the production of a optionally foamy fatty product of the kind described above (e.g. various types of shortening and whipped margarine) air or an inert gas is whipped into a heated liquid fat or liquid water-in-oil emulsion.

15 Thus, subsequent to suitable cooling and kneading a product having a soft texture at low temperatures (0°C-5°C) is obtained. Moreover, the whipping of air into fats for use as shortening serves to impart to the product an opaque, margarine-like appearance. The whipping of air or inert gas into margarine is effected in order to improve the frying
20 properties and the organoleptic properties of the margarine and to protect it from the formation of mould.

Apart from being used for baking and frying, margarine is used as a spread and for this particular purpose it is often produced from oils
25 containing polyunsaturated fatty acids which essentially consist of linoleic acid comprising two double bonds (18:2 n-6) and which less frequently have a low content of α -linolenic acid comprising three double bonds (18:3 n-3).

30 A disadvantage of the disclosed water-in-oil emulsion is that oxygen is introduced into the fatty product in the water phase. Dissolved oxygen in the water phase reduces the shelf life of fatty products containing polyunsaturated fatty acids considerably, because polyunsaturated fatty acids having more than two double bonds are very easily
35 oxidized, and the existing technology does not disclose how to produce a margarine emulsion in an oxygen-deficient environment. Thus, up till now, it has been impossible to produce a non-liquid fatty spread having a long shelf life and an increased content of polyunsaturated fatty acids of the n-3 series comprising at least 4 double bonds or of

the n-6 series comprising at least 3 double bonds.

This is unfortunate since a series of tests carried out in the past 20 years or so (Dyerberg, J., Linolenate-derived Polyunsaturated Fatty
5 Acids and Prevention of Atherosclerosis, Nutrition Reviews, vol. 44,
No. 4, 1986, pp 125-134) have shown that a daily intake of a few gram-
mes of i.a. polyunsaturated fatty acids comprising 5 double bonds
(20:5 n-3 and 22:5 n-3), which are mainly present in marine oils, par-
10 ticularly fish oils, and in phyto-plankton and algae, reduces the cho-
lesterol content of the blood and the risk of developing heart and
vascular disorders by virtue of their conversion into the physiologi-
cally active prostaglandin E_3 (PGE_3).

The intake of linoleic acid (18:2 n-6) alone, which has two double
15 bonds and which is converted slowly in the organism into the physio-
logically active prostaglandins PGE_1 and PGE_2 , is frequently not suf-
ficient to obtain a corresponding effect because the first step which
comprises the conversion of linoleic acid into γ -linolenic acid is
20 catalysed by the enzyme δ -6-desaturase which frequently has low acti-
vity in man (Hassam, A.G., The Role of Evening Primrose Oil Nutrition
and Disease., Jn: The Role of Fats in Human Nutrition, Ellis Horwood
Limited, Chicester, 1985, pp 84-100). γ -Linolenic acid (18:3 n-6),
which is present in vegetable oils such as evening primrose oil, bora-
25 ge oil and black-currant seed oil, is therefore a more efficient pre-
cursor in the biosynthesis of PGE_1 and PGE_2 (Gurr, M.J., Role of Fats
in Food and Nutrition, Elsevier Applied Science Publishers, London New
York, 1984, 170 pp), and this fact has led to a growing interest in
the use of γ -linolenic acid in i.a. food products.

30 However, it has not been possible to use commercially an amply occur-
ing raw material, such as fish oil and in particular sand eel oil hav-
ing a high content (about 15 percent by weight to about 30 percent by
weight) of n-3 fatty acids and vegetable oils, such as the above men-
tioned, having a high content (about 14 percent by weight to about 33
35 percent by weight) of n-6 fatty acids, in their unhydrogenated state
for the sake of the shelf life thereof, and thus the desirable nutri-
tive and wholesome effects thereof have not been fully utilized.

It is the object of the present invention to produce a stable and phy-

siologically active fatty product of the kind described above.

This object is achieved with the fatty product of the invention, which is characterized in that it is a water-in-oil emulsion or an oil-in-water emulsion containing at least 1 percent by weight of oxygen-deficient water and wherein the oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three double bonds. The water is rendered oxygen-deficient by e.g. sparging with inert gas, boiling out or by naturally containing inert gas.

By oxygen-deficient is understood that the amount of dissolved oxygen in the used water or water phase for the product of the invention is not sufficient to cause any substantial oxidation of the polyunsaturated fatty acids contained in said product.

It is surprisingly found that the highly unsaturated fatty acids are stabilized in a fatty product wherein the water phase is oxygen-deficient and into which inert gas and optionally a suitable amount of antioxidants have been whipped, thus imparting to the final product a peroxide number according to the IUPAC (2.501) of less than about 1 meq/kg.

Furthermore, the addition of preservatives, such as potassium sorbate, and antioxidants, such as alkylgallates, ascorbyl fatty acid esters and tocopherols, affords further improvement of the durability of the products according to the invention and, additionally, the antioxidants also aid in the protection of the fatty acids against oxidation occurring in the organism.

In one preferred embodiment of the invention mineral water, which is naturally carbonized water, is used for the water phase, which may further contain salt, flavours, milk solids, and thickeners, such as gelatin, alginate, and guar gum. An emulsion is prepared by adding the water phase to a mixture of heated fats and oils containing an emulsifier, such as a monodiglyceride of a fatty acid or a lecithine, and subsequently whipping the emulsion with an inert gas in an oxygenfree atmosphere. The whipped emulsion, which is of margarine type, is cool-

ed and packed.

5 In fatty products of the invention consisting of a water-in-oil emulsion the solid fat proportion at the storage temperature of the total fat and oil content is preferably not less than 10 percent by weight in order to obtain a non-liquid product and retain the whipped-in inert gas. Alternatively the oil phase can be reduced by using a suitable amount of thickener and/or gelling agent to obtain a non-liquid product.

10

In another preferred embodiment of the invention an oil-in-water emulsion is prepared by adding oil to a mixture of N_2 -sparged water and emulsifier. Vinegar may finally be added to obtain a mayonnaise-like product, which preferably is packed in air-tight containers.

15

For products of the invention consisting of an oil-in-water emulsion, such as mayonnaise, wherein the oil raw material is liquid at storage temperature, no solid fat is necessary in order to retain the whipped-in inert gas.

20

A preferred content of inert gas, such as N_2 , in the fatty product corresponds to 15 percent by volume.

25 The invention further relates to a process for the production of a non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant, wherein the inert gas is whipped into an oil-in-water emulsion or a water-in-oil emulsion wherein the oil phase comprises a mixture of fatty substances which was initially softened by heating and wherein the product thus produced is cooled. The process is characterized in using a mixture of fatty substances containing at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least three
30 double bonds and at least 1 percent by weight of oxygen-deficient
35 water.

The products produced in the process according to the invention may be packaged like similar products containing polyunsaturated fatty acids

comprising two double bonds and having a low content of polyunsaturated fatty acids comprising three or more double bonds.

5 In the following examples the invention will be described in further detail.

Example 1

10 A water phase (10 percent by weight of mineral water (naturally carbonized water)), 0.02 percent by weight of flavouring 2807, and antioxidants (propylgallate 100 ppm, ascorbylpalmitate 43 ppm, α -tocopherol 1000 ppm) is added while stirring to a preheated (40^oC-80^oC) mixture of 89.6 percent by weight of fat blend (10 parts soya m.p. 41^oC, 40 parts soya m.p. 35^oC, 30 parts soya oil, and 20 parts fish oil), 0.2 percent by weight of soya lecithin, 0.2 percent by weight of DIMODAN PV (mono- and diglyceride emulsifier) and 0.02 percent by weight of flavouring 3090. The water-in-oil emulsion having a temperature of about 45^oC is then cooled to 4^oC by passage through a one-pipe pilot plant of the Gerstenberg and Agger type. Gaseous nitrogen is introduced into the suction part of the high-pressure pump via a distribution nozzle to obtain a final product having a nitrogen content of 15 percent by volume. The product is filled into cups immediately upon the pipe cooler treatment. The final product is stored at a maximum temperature of 10^oC.

25

The fatty acid composition of the fish oil is as follows:

	<u>Fatty acid</u>	<u>percent by weight</u>
30	C 14:0	8.0
	C 15:0	0.3
	C 16:0	17.4
	C 16:1	9.5
35	C 16:2	0.6
	C 18:0	1.2
	C 18:1	9.1

	<u>Fatty acid</u>	<u>percent by weight</u>
	C 16:4	0.5
	C 18:2	1.9
5	C 18:3+20:1	8.9
	C 18:4+n-3	3.9
	C 22:1	13.3
	C 20:4 n-3	0.7
10	C 20:5 n-3	10.5
	C 24:1	1.6
	C 22:4	0.8
	C 22:5 n-3	0.8
15	C 22:6 n-3	9.4

In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour. The peroxide number was below 1 meq/kg after 4 weeks. In Denmark the accepted maximum period of storage for vegetable oil margarines is 7 weeks at temperatures below 10°C.

Example 2

25 A water phase (10 percent by weight of boiled mineral water, 0.02 percent by weight of flavouring 2807, and antioxidants (propylgallate 100 ppm, ascorbylpalmitate 43 ppm, α -tocopherol 1000 ppm) is added while stirring to a preheated (40°C-80°C) mixture of 89.6 percent by weight of fat blend (10 parts soya m.p. 41°C, 40 parts soya m.p. 35°C, 30
30 parts soya oil, and 20 parts fish oil), 0.2 percent by weight of soya lecithin, 0.2 percent by weight of DIMODAN PV (mono- and diglyceride emulsifier) and 0.02 percent by weight of flavouring 3090. The water-in-oil emulsion having a temperature of about 45°C is then cooled to 4°C by passage through a one-pipe pilot plant of the Gerstenberg and
35 Agger type. Gaseous nitrogen is introduced into the suction part of the high-pressure pump via a distribution nozzle to obtain a final product having a nitrogen content of 15 percent by weight. The product is filled into airtight plastic cups immediately upon the pipe cooler treatment. The final product is stored at a maximum temperature of

10°C.

The fish oil had the same composition as in Example 1.

5 In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour. The peroxide number was below 1 meq/kg after 4 weeks. In Denmark the accepted maximum period of storage for vegetable oil margarines is 7 weeks at temperatures below 10°C.

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Example 3

A mayonnaise-type product is produced from the following ingredients:

15	<u>Ingredients</u>	<u>Percent by weight</u>	
	Fish Oil*	10,0	* same composition
	Rapeseed oil	70,0	as in Examples 1
	Vinegar	1,5	and 2.
20	Egg yolks	4,0-6,0	
	Thickener	0,3	
	Salt	0,3	
	Flavour	0,02	
25	Water, preser- vatives, etc., up to	100	

30 Mineral water is poured into a mayonnaise plant, emulsifying turbine, or the like and egg yolks are added. Then the oil including dispersed thickener, salt, and preservatives are added continuously. Finally vinegar is added. The product is whipped with inert gas before being packaged in air-tight bottles.

In an accelerated storage experiment this product was stored at 25°C for 4 weeks without developing any off-flavour.

35

C l a i m s

1. A non-liquid fatty product containing an inert gas, at least one polyunsaturated fatty acid, water and optionally an antioxidant,
5 c h a r a c t e r i z e d in that the fatty product is a water-in-oil emulsion or an oil-in-water emulsion containing at least 1 percent by weight of oxygen-deficient water and wherein the oil phase contains at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 per-
10 cent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least 3 double bonds.
2. A fatty product according to claim 1, c h a r a c t e r i z e d in that it comprises at least 1 percent by weight of a polyunsaturated
15 fatty acid of the n-3 series comprising 5 double bonds, preferably eicosapentaenoic acid (10:5 n-3).
3. A fatty product according to claim 1, c h a r a c t e r i z e d in that it comprises at least 0.5 percent by weight of a polyunsaturated
20 fatty acid of the n-6 series comprising at least three double bonds, preferably γ -linolenic acid (18:3 n-6).
4. A fatty product according to claim 1, c h a r a c t e r i z e d in that it contains from about 10 percent by weight to about 85 percent
25 by weight of refined fish oil.
5. A fatty product according to claim 1, c h a r a c t e r i z e d in that it comprises a water-in-oil emulsion in which the water phase constitutes from 1 to 80 percent by weight and in which the oil phase
30 constitutes from 20 to 99 percent by weight, the oil phase containing at least 10 percent by weight of solid fat.
6. A fatty product according to claim 1, c h a r a c t e r i z e d in that it comprises an oil-in-water emulsion in which the water phase
35 constitutes from 1 to 80 percent by weight and in which the oil phase constitutes from 20 to 99 percent by weight.
7. A process for the production of a non-liquid fatty product contain-
ing an inert gas, at least one polyunsaturated fatty acid, water and

optionally an antioxidant, wherein the inert gas is whipped into an oil-in-water emulsion or a water-in-oil emulsion wherein the oil phase comprises a mixture of fatty substances which was initially softened by heating and wherein the product thus produced is cooled, c h a r -
5 a c t e r i z e d in using a mixture of fatty substances containing at least 1 percent by weight of a polyunsaturated fatty acid of the n-3 series comprising at least four double bonds and/or at least 0.5 percent by weight of a polyunsaturated fatty acid of the n-6 series comprising at least 3 double bonds and at least 1 percent by weight of
10 oxygen-deficient water.

8. Process according to claim 7, c h a r a c t e r i z e d in using a mixture of fatty substances containing at least 0.5 percent by weight of polyunsaturated fatty acids of the n-6 series comprising at least 3
15 double bonds, preferably γ -linolenic acid.

9. Process according to claim 7, c h a r a c t e r i z e d in using a mixture of fatty substances containing from about 10 to about 85 per-
20 cent by weight of refined fish oil.

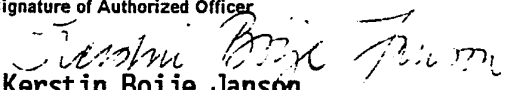
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INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 91/00017

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: A 23 D 7/00, 02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	A 23 D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,A	EP, A1, 0395569 (KATBORG, JON) 31 October 1990, see the whole document --	1-9
A	EP, A1, 0319360 (VERNIN, JEAN-GILLES) 7 June 1989, see the whole document --	1-9
A	EP, A2, 0304115 (UNILEVER NV) 22 February 1989, see the whole document --	1-9
A	US, A, 4764392 (YASUFUKU ET AL) 16 August 1988, see the whole document --	1-9
A	EP, A2, 0285198 (UNILEVER NV) 5 October 1988, see the whole document --	1-9
<p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19th April 1991	1991 -04- 24	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	 Kerstin Boije Janson	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	FR, A, 573718 (M. PETER MÖLLER HEYERDAHL) 28 June 1924, see the whole document -- -----	1-9

91-03-23

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 91/00017**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 91-03-23. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0395569	90-10-31	AU-D- 5630690 WO-A- 90/12510	90-11-16 90-11-01
EP-A1- 0319360	89-06-07	FR-A- 2623692	89-06-02
EP-A2- 0304115	89-02-22	AU-D- 2028088 JP-A- 1067152	89-02-09 89-03-13
US-A- 4764392	88-08-16	NONE	
EP-A2- 0285198	88-10-05	AU-D- 1316688 JP-A- 63267232 US-A- 4874626	88-09-22 88-11-04 89-10-17
FR-A- 573718	24-06-28	NONE	