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NOTICE OF ENTITLEMENT
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670336

I, LODERS-CROKLAAN B.V.
of Zaandijkerweg 36, 1521 AX Wormerveer, The Netherlands,
being the applicant in respect of Application No. _____,
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, state the

Part 1 - Must be completed for all applications.

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"The present applicant is the assignee of Unilever PLC, and Unilever PLC was the assignee of the employer of the actual inventors, namely UNILEVER UK CENTRAL RESOURCES LIMITED. UNILEVER UK CENTRAL RESOURCES LIMITED was entitled to have assigned to it a patent granted to any of the actual inventors in respect of the said invention".

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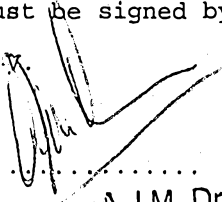
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applicant or patentee of the main invention.

I,
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authorise

to apply for a further patent for an improvement in, or modification of, the main
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Note: This part must be signed by the applicant/patentee of the main invention.

LODERS CROKLAAN B.V.



A.J.M. Dries

(Signature) (authorised signatory)

23 March 1995

(Date)

* Omit/Delete if not appropriate



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- (71) Applicant(s)
LODERS-CROKLAAN B.V.
- (72) Inventor(s)
JOHN BERNARD HARRIS; STEPHEN RAYMOND MOORE; CHRISTOPHER RAWLINS
- (74) Attorney or Agent
UNILEVER AUSTRALIA LIMITED , B F Jones, Private Mailbag 2, EPPING NSW 2121
- (56) Prior Art Documents
EP 81881
WO 83/00418
US 3492130
- (57) Claim

1. A process for preparing a fat fraction, suitable as fat component in non-lauric, non-hydrogenated, cool-melting, non-temper, non-trans filling or coating fats characterised by: performing a fractionation on a triglyceride composition, containing at least 5 wt% SSU triglycerides (S= saturated fatty acid C₁₆-C₂₂; U- mono- or poly-unsaturated fatty acids C₁₈-C₂₂), removing at least part of the trisaturated triglycerides and/or at least part of the di- and tri-unsaturated triglycerides and isolating a triglyceride composition with an SSU content of at least 12 wt%, preferably 12-20 wt%, which content is at least 1.5 times, preferably at least 1.7 times, most preferably at least 2 times the SSU content of the starting triglyceride composition.
5. Process according to claim 1, wherein a palm oil stearin is fractionated in two steps.

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(10) 670336

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7. Process according to claims 5 or 6, wherein the fractionation comprises the following steps:
 - 1) a wet fractionation of the palm oil stearin with an organic solvent at -5 to 5°C, yielding a stearin fraction, consisting predominantly of SSS, SUS and SSU triglycerides.
 - 2) a wet fractionation of the stearin fraction of 1) with an organic solvent at 15-25°C and collecting the olein fraction as the product, enriched in SSU.



IN

<p>(51) International Patent Classification ⁵ : C11B 7/00, A23D 9/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/09098 (43) International Publication Date: 28 April 1994 (28.04.94)</p>
<p>(21) International Application Number: PCT/EP93/02776 (22) International Filing Date: 8 October 1993 (08.10.93) (30) Priority data: 92309489.0 16 October 1992 (16.10.92) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except US): LODERS-CROKLAAN B.V. [NL/NL]; Zaanijkeweg 36, NL-1521 AX Wormerveer (NL). (72) Inventors; and (75) Inventors/Applicants (for US only) : HARRIS, John, Bernard [GB/GB]; 20 Colworth Road, Sharnbrook, Bedford MK44 1ET (GB). MOORE, Stephen, Raymond [GB/GB]; 2 Wainwright Avenue, Thrapston NN14 4UH (GB). RAWLINS, Christopher [GB/GB]; 9 Baker Close, Rushden, Northants NN10 0EJ (GB).</p>		<p>(74) Agent: SIKKEN, Antonius, J., H., M.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.</p> <p style="text-align: center; font-size: 2em; font-weight: bold;">670336</p>
<p>(54) Title: TRIGLYCERIDE FRACTIONATION</p> <p>(57) Abstract</p> <p>The invention concerns a fractionation process for the production of triglycerides with at least 12 wt% SSU (S = saturated fatty acids; U = unsaturated fatty acids) by subjecting a fat with at least 5 wt% SSU to a fractionation, achieving an enrichment factor for the SSU enrichment of at least 1.5.</p>		

Triglyceride fractionation

In British patent application 9121578.0 we have disclosed non-temper confectionery fats, containing minimal working
5 amounts of fat of the SSO-type. These fat compositions are obtained by adding externally the working amount of SSO.

Above method has, however, the disadvantage that we must have free access to SSO-type triglycerides. Although
10 several methods are known by which these fats can be synthesized, it would offer a main advantage when triglyceride mixtures could be obtained along non-synthetic routes, e.g. by applying fractionation techniques only, that contain enough of the SSO component to make them
15 suitable as additive for polymorphic fats that otherwise needed tempering. Even more advantages could be achieved when fat mixtures could be obtained that do not need to be tempered anymore, because of the presence of enough of the SSO triglycerides.

20

In fact, our invention concerns with a process that results in the production of the desired fat mixtures. Therefore, our invention concerns a process for preparing a fat fraction, suitable as fat component in non-lauric, non-
25 hydrogenated, cool melting, non-temper, non-trans filling or coating fats. This process is characterized by: performing a fractionation on a triglyceride composition, containing at least 5 wt% SSU triglycerides (S= C₁₆-C₂₂ saturated fatty acid, preferably C₁₆-C₁₈; U= mono- or poly-
30 unsaturated C₁₈-C₂₂ fatty acid; preferably oleic acid), removing at least part of the trisaturated triglycerides and/or at least part of the di- and tri-unsaturated triglycerides and isolating a triglyceride composition with an SSU content of at least 12 wt%, preferably 12-20 wt%,
35 which content is at least 1.5 times, preferably at least 1.7 times, most preferably at least 2.0 times the SSU content of the starting triglycerides composition.

Simultaneously, the SUS content of the products isolated should be at least 65 wt%, preferably at least 70 wt%.

The starting triglyceride, preferably contains at least 6
5 wt% of the SSU triglycerides. As the endproducts are meant to be used as confectionery fats, the starting fats are also rich in SUS-triglycerides. Suitable fats, meeting above criteria are: palm oil, palm oil fractions, mixtures thereof, in particular palm oil stearin, and more
10 particularly a palm oil stearin, obtained after dry fractionation. Very useful results can be obtained by using mixtures of palm oil and dry fractionated palm oil stearin, in particular mixtures with more than 20 wt% of the stearin.

15

From EP 81 881 a process is known, wherein a palm oil stearin is subjected to a solvent fractionation. Three fractions are obtained, i.e. a first fraction with a melting point above 45°C, a second fraction with a melting
20 point between 33 and 44°C and a third, liquid fraction. The fractionation is performed by mixing 1-6 l of solvent per gram of fat at 50°C; cooling the solution obtained to 12-14°C, collecting the precipitate formed; extracting said precipitate under specific conditions with solvent of 10°C;
25 filtering the slurry from the extraction step, resulting in the high melting product and a filtrate; the filtrate is cooled to 1-3°C and the new precipitate is collected; this new precipitate is extracted again under very specific conditions; after filtering of the slurry of this second
30 extraction the intermediate melting product is separated, the filtrate also obtained is subjected to a removal of the solvent giving the liquid oil. According to page 9, lines 22-42 the extraction steps are incomparable with washing steps and have main advantages over a washing. Nothing is
35 disclosed about the SSU-content of the starting palm oil stearin, the SSU content of the end products, enrichment in the SSU content or the production of non-temper

confectionery fats. In our process we do not apply the very specific extraction (= non-washing) steps, as prescribed by the above EP 81 881.

5 Wet fractionations of palm oil-based materials are known from a.o. DE 2,921,499; DE 1,792,606; US 3,686,240; US 4,055,679; EP 347,006 or EP 78,568. However, in none of these references it is mentioned that the product obtained has an SSU-content of at least 12 wt%, while an enrichment
10 with a factor 1.5 for the SSU-content is achieved.

The fractionation can be carried out as dry fractionation, or as wet fractionation, while also combinations of these two can be applied. In case a dry fractionation is
15 performed, we prefer to perform a multi-step dry fractionation as disclosed in our European Patent application 399 597.

Depending on the type of starting material the fractionation can be a two-step or a multi-step
20 fractionation process.

The best results are obtained, when we apply a two-step wet fractionation process.

25 In a two-step process, starting from palm oil stearin the following steps can be applied:

1. wet fractionation with an organic solvent, such as hexane, petr. ether and in particular acetone, at -5 to 5°C, yielding a stearin fraction, preferably in
30 yields of 45-85 wt%, more preferably 45-75 wt% based on the palm oil stearin. This fraction predominantly consists of SSS, SUS and SSU triglycerides.
2. The stearin fraction of 1) is subjected to a second wet fractionation with an organic solvent (again
35 hexane, petr. ether or acetone) at 15-25°C. This time the olein (or bottom) fraction is collected as the product enriched in SSU (at least 12 wt%). This

olein fraction is separated in a yield of 25-80 wt%, preferably 35-80 wt%, based on the stearin fraction of step 1).

5 An alternative route, however, is to perform the first wet fractionation at 15-25°C, collecting the olein fraction, consisting predominantly of UUU; SUU; SSU and SUS triglycerides. Subjecting this olein fraction to a second wet fractionation at -5 to 5°C and collecting the stearin
10 fraction as product fraction.

In this case the olein fraction is separated in the first step in a yield of 45-90 wt%, preferably 55-85 wt%, while the stearin fraction in the second stage is separated in a
15 yield of 25-80 wt%, preferably 40-50 wt%.

In the wet fractionation amounts of 1-8, preferably 3-7 l solvent per kg triglyceride material are used. The exact amount will vary with the type of solvent and with the
20 fractionation temperature applied.

Working within the process parameter set out above will in general result in a product with at least 12 wt% SSU, whereas the ratio between the weight content SSU in the
25 product and the weight content of SSU in starting material is at least 1.5. Simultaneously, its SUS content will be more than 65 wt%.

Although wet fractionation steps are disclosed in detail
30 above, dry fractionation steps, in particular as a multi-step process, can also be applied.

The products resulting from the process are very suitable for application in the fat part of fillings or coatings of
35 confectionery products, such as chocolate bars or bonbons. The use of these compounds will impart cool melting and

non-temper properties to the filling or coating compositions of the confectionery product.

Example

5

Four different triglyceride compositions A, B, C and D with the composition mentined in table I were subjected to a double wet fractionation.

The conditions for the wet fractionations are given in
10 table II. The olein fractions of step 2 were collected.
Their SSU content is given in table III.

Table I

15

	SSS	SOS	SSO	SLns	SSLn	SOO	OSO	SOLn	OOO	> 3DB
A	27.8	30.5	7.1	6.0	1.2	15.0	1.7	5.7	2.0	2.7
B	17.3	32.5	5.9	7.4	1.4	20.9	0.9	7.8	2.6	3.2
C	11.0	33.7	5.2	8.2	1.5	24.4	0.3	9.1	2.9	3.4
D	6.8	34.5	4.7	8.8	1.6	26.8	0.0	9.9	3.1	3.6

20

S= saturated C₁₆/C₁₈

O= oleic

Ln= linoleic

DB= double bonds

25



Table II

	<u>solvent</u>	<u>l solv/kg</u> <u>TG</u>	<u>fract T</u>	<u>prod. fr.</u>	<u>yield</u> <u>pr.fr.*</u>
step 1	acetone	6.0	0°C	stearin	45%
5 step 2	acetone	6.0	20°C	olein	35%

* based on starting material

Table III

	SSU in start. fat	% SSU in end product
10 Fat A	8.3	14.3
B	7.3	12.4
C	7.7	13.2
D	6.3	10.8

15 It will be evident from the above results that although starting material D meets the requirement of SSU content, the product obtained from this material D is too low in SSU. This means that other yields or temperatures must be applied for this fat, when one wants to cope with the SSU
20 content of the end product.

Comparative example

Example 1 of EP 81 881 was carried out, starting from a
25 palm oil stearin with the following triglyceride composition:

S ₃	:	30.3 wt%	SLnS	:	6.6 wt%
SOS	:	29.1	SSLn	:	1.8
SSO	:	7.3	SOO	:	13.9

30

OSO	:	1.3 wt%
SOLn	:	5.4
O ₃	:	2.0

The conditions, mentioned in EP 81 881 were used. A product enriched in SSU was obtained. This product had the following composition:

5	S ₃	:	1.9 wt%	SLnS	:	7.9 wt%
	SOS	:	58.9	SSLn	:	1.4
	SSO	:	11.5	SOO	:	10.4
	OSO	:	1.0 wt%			
10	SOLn	:	3.6			
	O ₃	:	1.5			

So, in this process we could not achieve an enrichment in the SSU-component of more than 1.5 (found: 1.41). Moreover, 15 the SUS content of this fraction was rather low (66.8 wt%).

CLAIMS

1. A process for preparing a fat fraction, suitable as fat component in non-lauric, non-hydrogenated, cool-melting, non-temper, non-trans filling or coating fats characterised by: performing a fractionation on a triglyceride composition, containing at least 5 wt% SSU triglycerides (S= saturated fatty acid C₁₆-C₂₂; U- mono- or poly-unsaturated fatty acids C₁₈-C₂₂), removing at least part of the trisaturated triglycerides and/or at least part of the di- and tri-unsaturated triglycerides and isolating a triglyceride composition with an SSU content of at least 12 wt%, preferably 12-20 wt%, which content is at least 1.5 times, preferably at least 1.7 times, most preferably at least 2 times the SSU content of the starting triglyceride composition.
2. Process according to claim 1, wherein the SSU content of the starting triglyceride composition is at least 6 wt%.
3. Process according to claim 1, wherein the SUS content (S and U identical with S and U of claim 1) of the product isolated is at least 65 wt%, preferably at least 70 wt%.
4. Process according to claims 1 or 2, wherein the starting triglyceride composition is palm oil, fractions of palm oil or mixtures thereof, in particular a stearin fraction of palm oil, especially a stearin fraction obtained after dry fractionation of palm oil.
5. Process according to claim 1, wherein a palm oil stearin is fractionated in two steps.

6. Process according to claim 5, wherein the two steps both comprise wet fractionation.
7. Process according to claims 5 or 6, wherein the fractionation comprises the following steps:
 - 1) a wet fractionation of the palm oil stearin with an organic solvent at -5 to 5°C, yielding a stearin fraction, consisting predominantly of SSS, SUS and SSU triglycerides.
 - 2) a wet fractionation of the stearin fraction of 1) with an organic solvent at 15-25°C and collecting the olein fraction as the product, enriched in SSU.
8. Process according to claim 7, wherein the stearin fraction of step 1) is separated in a yield of 45-85 wt%, preferably 45-75 wt%, based on the palm oil stearin, while the olein fraction of step 2) is separated in a yield of 25-80 wt%, preferably 35-80 wt%, based on the stearin fraction of step 1).
9. Process according to claims 5 or 6, wherein the fractionation comprises the following steps:
 - 1) a wet fractionation of the palm oil stearin with an organic solvent at 15-25°C separating an olein fraction, consisting predominantly of U₃; SUU; SSU and SUS-triglycerides
 - 2) a wet fractionation of the olein fraction of 1) with an organic solvent at -5 to 5°C and collecting the stearin fraction as the product, enriched in SSU.
10. Process according to claim 9, wherein the olein fraction of step 1) is separated in a yield of 45-90 wt%, preferably 55-85 wt%, based on the palm oil stearin, while the stearin fraction of step 2) is separated in a yield of 25-80 wt%, preferably 40-50 wt%, based on the olein fraction step 1).

11. Process according to claims 6-10, wherein the wet fractionations are carried out, using hexane, petroleum ether or preferably acetone as solvent in amounts of 1-8 l per kg triglyceride.
12. Filling- or coating compositions for confectionery products, wherein part of the fat component is a fat, obtainable according to the process of claims 1-11.
13. Use of a triglyceride composition, containing SSU-type triglycerides in confectionery fats, characterised in that the triglyceride compositions, obtainable according to the process of claims 1-11 are used to impart cool melting, non-temper properties to the filling or coating composition of a confectionery product.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/02776

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11B7/00 A23D9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11B A23D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 081 881 (SOCIETE DES PRODUITS NESTLE S.A.) 22 June 1983 see page 2, line 7-10; claims 1,2,9,10,12; example 1; table B see page 1, line 13 - line 20 see page 5, line 29 - line 35 ---	1,2,4-6, 9-12
A	WO,A,83 00418 (SCM CORPORATION) 17 February 1983 see claims 1,3,4; figure 2; example 4 ---	1,4-8,12
A	US,A,3 492 130 (J. HARWOOD) 27 January 1970 see column 2, line 59 - line 71; claims 1-6 see column 1, line 58 - line 68 ---	1,12
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
 - *E* earlier document but published on or after the international filing date
 - *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)
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Date of the actual completion of the international search 11 January 1994	Date of mailing of the international search report 18. 01. 94
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Kanbier, D
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/02776

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 303 072 (UNILEVER NV) 1 October 1976 see page 4, line 36 - line 40; claim 1; examples D,F -----	1,2,4

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 93/02776

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-A- 8827482	22-02-83
		CA-A- 1199830	28-01-86
		DE-T- 3248922	19-04-84
		EP-A- 0085096	10-08-83

US-A-3492130	27-01-70	NONE	

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