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(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **BE DE FR NL**

Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
(84) **GB**

(72) Inventor: **Van den Broek, Will J.**
Bayensweer 43
NL-3371 PA Hardingsveld-Giessendam(NL)
Inventor: **Van de Sande, Robert Leo K.M. c/o**
Unilever Res.
Olivier van Noortlaan 120
NL-3133 AT Vlaardingen(NL)
Inventor: **Segers, Jacobus Cornelis c/o**
Unilever Research
Olivier van Noortlaan 120
NL 3133 AT Vlaardingen(NL)

(74) Representative: **Mulder, Cornelis Willem**
Reinier, Dr. et al
UNILEVER N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) Method of refining glyceride oil.

(57) The invention pertains to a method of refining glyceride oil comprising (1) an acid treatment in which an acid or acid anhydride is dispersed in the oil, (2) a hydration treatment in which alkali is mixed into the acidified glyceride oil during which treatment the temperature is maintained at 70° C or less, and (3) a separation treatment in which hydrated phosphatides so formed are separated from the glyceride oil. The invention provides a method to reliably achieve very good degumming results.

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The present invention relates to a method of refining glyceride oil, and in particular to such a method comprising an acid treatment in which an acid or acid anhydride is dispersed in the oil, a hydration treatment in which alkali is mixed into the acidified glyceride oil and a separation treatment in which hydrated phosphatides so formed are separated from the glyceride oil.

Glyceride oils of in particular vegetable origin, such as soybean oil, rapeseed oil, sunflower oil, safflower oil, cotton seed oil and the like, are a valuable raw material for the food industries. These oils in crude form are usually obtained from seeds and beans by pressing and/or extraction.

Such crude glyceride oils mainly consist of triglyceride components. However, they generally also contain a significant amount of non-triglyceride components including phosphatides (gums), waxy substances, partial glycerides, free fatty acids, colouring materials and small amounts of metals. Depending on the intended use of the oil, many of these impurities have an undesirable effect on the (storage) stability, taste, and colour of later products. It is therefore necessary to refine, i.e. to remove the gums and other impurities from the crude glyceride oils as much as possible.

In general the first step in the refining of glyceride oils is the so-called degumming step, i.e. the removal of the gums. In this context the term "degumming" relates to any treatment which eventually results in the removal of gums and associated components from the oil. In conventional degumming processes water is added to the crude glyceride oil to hydrate the phosphatides, which are subsequently removed, e.g. by centrifugal separation. Since the resulting degummed oil often still contains unacceptably high levels of "non-hydratable" phosphatides, this water-degumming step is normally followed by chemical treatments with acid and/or alkali to remove the residual phosphatides and to neutralize the free fatty acids ("alkali-refining").

Subsequently, the soapstock so formed is separated from the neutralized oil by for instance centrifugal separation. The resulting oil is then further refined using bleaching and deodorizing treatments.

By the above-described water-degumming step in general residual phosphorus levels are achieved in the order of 100-250 ppm. US-A-4,049,686 discloses an improved refining method in which the crude or water-degummed oil is treated with a concentrated acid such as in particular citric acid, reducing residual phosphorus levels to within the range of from 20 to 50 ppm.

EP-A-195,991 discloses a process for producing degummed vegetable oils, in which water degummed oil is first subjected to an acid treatment in which acid is finely dispersed in the water-degummed oil under dispersion conditions yielding at least 10 million acid droplets per gram of oil corresponding to an interface surface area between the acid and oil droplets of at least 0.2 m^2 per 100 gram of oil, and subsequently, to an alkali treatment in which sufficient alkali is added to the acid-in-oil dispersion to increase the pH to above 2.5. The refining process is carried out at an oil temperature of more than 75 ° C.

The above prior-art refining process is characterized by a difficult separation step requiring a large number of centrifuges (EP-A-344,718). Moreover, for certain oil qualities residual phosphorus levels are obtained that are still unacceptably high.

A review of prior-art refining processes is given in the article by J.C. Segers and R.L.K.M. van der Sande, entitled "Degumming - Theory and Practice", and presented at the AOS World Conference on Edible Oils and Fats, 2-6 October 1989, Maastricht, the Netherlands.

It is therefore an object of the present invention to provide a refining process which does not require the severe dispersion conditions of the aforementioned prior-art refining process.

It is a further object of the present invention to provide a refining process which reliably achieves very low levels of residual phosphatide and other impurities.

It is still a further object to provide a refining process in which the removal of gums is less cumbersome than in the aforementioned prior-art refining process.

The present invention now provides a method of refining glyceride oil comprising an acid treatment in which an acid or acid anhydride is dispersed in the oil, a hydration treatment in which alkali is mixed into the acidified glyceride oil and a separation treatment in which hydrated phosphatides so formed are separated from the glyceride oil, characterized in that during the hydration treatment the hydration temperature is equal to or below 70 ° C.

An essential aspect of the invention is that during the hydration treatment the hydration temperature is equal to or below 70 ° C. At higher temperatures the hydrated phosphatides formed are of such nature that they are to a lesser extent, and in some cases even not at all, removable from the oil.

The hydration of the phosphatides and their removal from the oil is positively affected by applying even lower hydration temperatures. Good degumming results are obtained at a hydration temperature of less than 60 ° C, preferably less than 40 ° C. Excellent refining results are obtained if the hydration temperature is maintained in the range of 10 to 50 ° C, preferably 20 to 30 ° C. In general, lower hydration temperatures allow less severe separation conditions, i.e. e.g. shorter centrifugation times and/or lower centrifugal forces may be applied in the separation treatment for obtaining excellent refining results.

In the hydration treatment the hydration time necessary for forming hydrated phosphatides that are removable from the oil, is dependent of the hydration temperature applied. At higher hydration temperatures shorter hydration times may be used. In general, the hydration time should be more than 3 minutes. Good results are obtained at hydration times of more than 30 minutes, preferably more than 50 minutes. Under practical conditions the hydration time is normally in the range of 30 to 240 minutes, preferably 60 to 240 minutes, most preferably in the range of 60 to 180 minutes.

The refining method of the invention is generally applicable to both crude (non-degummed) oil, and degummed oils. Whether it is best to use crude or degummed oil, is dependent on the composition of the phosphatides present in the oil. Sunflower oil and maize germ oil are examples of oils that may be refined by the method of the invention without prior degumming. Rapeseed oil and soybean oil are examples of oils which may need pre-degumming prior to application of the method in accordance with the invention. Although the oil may be predegummed by any suitable degumming process, normally it is sufficient that the oil is water degummed.

The acid or acid anhydride used in the acid treatment may be any acid or corresponding acid anhydride which converts the phosphatides into hydratable phosphatides. The acid or acid anhydride should be non-toxic, miscible with water, and may be of both inorganic and organic origin. Examples of suitable acids are phosphoric acid and citric acid. The use of citric acid is preferred.

The amount of acid or acid anhydride used should be such, that substantially all phosphatides present are converted in the hydratable form. In general, suitable amounts of acid lie in the range of 0.01 to 1 % by weight, preferably 0.01 to 0.5 % by weight of the glyceride oil. Citric acid is suitably added in an amount of 0.01 to 0.4 % by weight of the glyceride oil as a 50 % by weight aqueous citric acid solution. Phosphoric acid is suitably used in an amount of 0.02 to 0.4 % by weight, e.g. as a 35 % by weight aqueous phosphoric acid solution.

The conditions under which the acid is dispersed into the glyceride oil, may be less severe than the dispersion conditions disclosed in EP-A-195,991. Any static or dynamic mixer may be used suitable to achieve an acid-droplets distribution throughout the oil, said acid droplets generally having an average size in the range of from 10 to 20 micrometers.

The time during which the oil is in contact with the dispersed acid is not critical. During the acid treatment generally the oil temperature is as high as possible, and in practical circumstances is in the range of 60 to 95 °C, preferably 70 to 90 °C. However, it is essential that prior to the hydration treatment the oil is cooled to a temperature equal to or below 70 °C.

In the hydration treatment the amount of alkali added is such that the hydrated phosphatides formed can be easily removed from the oil. Dependent on the amount of acid used in the preceding acid treatment, the alkali is generally added in an amount sufficient to neutralize 10 to 200 % of the acid or acid anhydride added in the acid treatment. Preferably, the alkali is added in an amount sufficient to neutralize 25 to 100 % of the acid.

During the refining process in accordance with the invention the water content of the oil is such that the hydration of the phosphatides is not inhibited because of a shortage of water. Water may be added during any stage of the refining process up to the hydration treatment. Preferably, alkali and water are added simultaneously as an aqueous alkali solution. In the hydration treatment the water content of the oil is generally 0.5 to 5 % by weight, dependent on the phosphatide level in the oil to be refined.

Examples of alkali that may suitably be used in the hydration treatment are sodium hydroxide, potassium hydroxide and ammonia, which are generally added as the aqueous solutions thereof.

After the separation of the hydrated phosphatides and other impurities from the oil, which is preferably carried out by way of centrifuging, it is generally not necessary to subject the refined oil to a further water-washing treatment. Although a water-washing treatment further decreases the phosphorus level of the glyceride oil, this decrease is under the hydration conditions according to the present invention generally marginal and under circumstances may not counterbalance the required use of an additional separation treatment (centrifuge) or the extra amount of effluent involved.

The present invention is now further illustrated by way of the following examples.

Example 1

Batches of water-degummed (wdg) rapeseed and soybean oils were subjected to a refining process in accordance with the invention (method A; hydration temperature of 20 °C / hydration time of 120 minutes) and, for reasons of comparison, to a refining process according to EP-A-195,991 (method B: hydration temperature of 90 °C / hydration time of 3 minutes).

The batches were heated to 90° C and their water contents were adjusted to 0.6 % by weight. Amounts of 0.215 % by weight of concentrated phosphoric acid (85 wt.% aqueous solution) were added to the batches and dispersed in the oils using an Ultra-Turrax^{R} (mixing time 30 seconds). Subsequently, the mixtures were agitated for 2.5 minutes. Thereafter, amounts of 2.5 % by weight of a 5 wt.% aqueous solution of sodium hydroxide were added.

The batches were subjected to each of the hydration methods A and B, whereafter the hydrated phosphatides were removed by three different separation procedures.

According to separation I the hydrated phosphatides were removed by centrifuging for 10 minutes using a centrifugal force of about 100 g, and according to separation II by centrifuging for 45 minutes at about 850 g. The oils obtained after separation II were further subjected to a water washing with 2 % by weight of water whereafter the water layer was removed by centrifuging for 45 minutes at about 850 g (separation III).

The phosphorus and calcium levels of the wdg starting oils and the phosphorus levels of the oils after refining according to method A of the present invention and according to method B of EP-A-195,991 were measured and are indicated in Table 1.

From these analytical data it is concluded that when the refining process according to the invention (method A) is used in combination with the mild separation I, no significant correlation between the residual phosphorus level in the refined oil and the calcium level in the starting oil is found, whereas when the refining process according to EP-A-195,991 (method B) is used in combination with the severe separation III, the residual phosphorus level is positively correlated with the calcium level in the starting oil.

Accordingly, the refining process according to the invention is more reliable than that of EP-A-195,991.

Table 1

wdg oil			separation$^{2)}$					
			I		II		III	
type$^{1)}$	P (mg/kg)	Ca (mg/kg)	method$^{3)}$		method$^{3)}$		method$^{3)}$	
			A	B	A	B	A	B
rape	335	145	10	19	3	19	3	16
rape	229	160	15	-	-	80	-	73
rape	220	156	14	-	-	53	-	53
rape	180	85	8	21	4	21	3	3
bean	135	65	9	36	6	38	4	36
rape	128	98	17	-	-	35	-	32
rape	115	75	9	23	7	22	7	21
rape	112	63	6	-	-	15	-	8
rape	105	65	15	215	7	225	6	19
rape	88	69	15	-	-	27	-	21
bean	80	41	16	17	7	16	2	14

1) rape: rapeseed oil; bean: soybean oil
2) see text
3) A: alkali hydration temperature of 20°C / hydration time of 120 minutes (invention)
B: alkali hydration temperature of 90°C / hydration time of 3 minutes (EP-A-195,991)

Example 2

Two wdg rapeseed oils were used: oil (1) comprised 230 mg/kg P and 151 mg/kg Ca; and oil (2) comprised 220 mg/kg P and 148 mg/kg Ca. These wdg rapeseed oils were heated to 90° C and their water content was adjusted to 0.6 % by weight. Amounts of 0.215 % by weight concentrated phosphoric acid (85 wt.%) were added to the oils and dispersed in the oils using a Ultra-Turrax^{R} (mixing time 30 seconds).

Subsequently, the mixtures were agitated during 2.5 minutes. Thereafter, 2.5 % by weight of a 5 wt.% aqueous solution of sodium hydroxide was added. The hydration temperature T (°C) was varied between 8 and 90°C and the hydration time t (min.) was varied between 3 and 157 minutes. The hydrated phosphatides were removed from the oils by respectively separation I and separation III (see example 1). The residual phosphorus levels in the resulting oils were measured and are shown in Table 2.

The analytical data were subjected to a statistical analysis described in Experimental Designs, W.G. Cochran and G.M. Cox, Wiley (1957), Chapter 8A, "Some methods for the study of response surfaces", which analysis resulted for separation I in the response equation:

$$P(I) = \exp(2.45 + 0.387x_1 - 0.279x_2 + 0.7511x_1^2 + 0.6628x_1.x_2)$$

and for separation III in the response equation:

$$P(III) = \exp(1.881 + 1.049x_1 - 0.133x_2 + 0.0046x_1^2 + 0.1098x_1.x_2)$$

wherein

$x_1 = (T-49)/29$

$x_2 = (t^{\frac{1}{2}}-7.134)/3.82$

From the above response equations it is concluded that lowering of the hydration temperature (to 70°C or less) gives improved refining results. In order to obtain hydrated phosphatides that are well removable, it may be required to select longer hydration times (30 minutes or more).

Table 2

		t (min.)				
T (°C)	oil	3	11	51	120	157
separation I						
8	2			24.3		
20	1		52.5		7.5	
49	1			7.6		
49	1			22.0		
49	2	11.9		11.0		6.1
49	2			15.6		
78	1		26.0			
90	1	35.1				
90	2	33.7		102.5		
separation III						
8	2			1.8		
20	1		2.6		1.5	
49	1			6.4		
49	1			7.3		
49	2	7.2		5.8		4.9
49	2			9.6		
78	1		16.0		22.5	
90	1	33.1				
90	2	30.3		22.5		

Example 3

Wdg maize oil (oil 1), non-degummed sunflower oil (oil 2), two wdg soybean oils (oils 3 and 4) and wdg rapeseed oil (oil 5) were mixed with 0.2 % by weight of a 45 wt.% solution of citric monohydrate using an Ultra Turrax^R (30 seconds) followed by 10 minutes turbine stirring at 600 rpm, or with 0.1 % by weight of a 34 wt.% phosphoric acid solution using an Ultra Turrax^R (60 seconds). Subsequently, amounts of 2 % by weight 1 N sodium hydroxide solution were added to the oils under turbine stirring (10 minutes, 600 rpm). An alkali hydration temperature of 30° C was maintained two hours under turbine stirring at 300 rpm.

After completion of the hydration treatment the hydrated phosphatides were removed by centrifuge (10 minutes at 1000 rpm corresponding to about 100 g).

The phosphorous and Ca levels in the starting oils and the residual phosphorus levels in the refined oils are summarized in Table 3.

Table 3

Oil	before degumming		after degumming
type	P (mg/kg)	Ca (mg/kg)	P (mg/kg)
1	90	1	17
2	128	22	9
3	102	35	13
4	100	45	4
5	142	100	3

Example 4

Non-degummed maize germ oil heated to 70° C was mixed with 0.1 % by weight citric monohydrate. Thereafter, the oil was cooled to 20° C and at this temperature 2 % by weight of an aqueous sodium hydroxide solution was added in an amount sufficient to neutralise 2/3 of the citric acid present in the oil. After two hours at 20° C the hydrated phosphatides were removed by centrifuge (10 minutes at 1000 rpm corresponding to about 100 g).

Analytical data of the starting and refined oil are shown in Table 4.

Table 4

Oil	P (mg/kg)	Ca/Mg (mg/kg)	Fe (mg/kg)	Na (mg/kg)	ffa (wt%)
crude	375	1.4/46	3.1	8.9	2.00
refined	16	0.3/0.9	0.2	5.0	1.73

Claims

1. Method of refining glyceride oil comprising an acid treatment in which an acid or acid anhydride is dispersed in the oil, a hydration treatment in which alkali is mixed into the acidified glyceride oil and a separation treatment in which hydrated phosphatides so formed are separated from the glyceride oil, characterized in that during the hydration treatment the hydration temperature is equal to or below

70° C.

2. Method according to claim 1 wherein the hydration temperature is equal to or below 40° C.

3. Method according to claim 2 wherein the hydration temperature is in the range of 20 to 40° C.

4. Method according to any one of the preceding claims wherein in the hydration treatment the hydration time is more than 3 minutes.

5. Method according to claim 4 wherein the hydration time is in the range of 30 to 240 minutes, preferably 60 to 180 minutes.

6. Method according to any one of the preceding claims wherein the glyceride oil is a degummed glyceride oil.

7. Method according to any one of the preceding claims wherein in the acid treatment the acid or acid anhydride is added in an amount of 0.01 to 1 % by weight, preferably 0.01 to 0.5 % by weight of the glyceride oil.

8. Method according to any one of the preceding claims wherein in the hydration treatment alkali is added in an amount sufficient to neutralize 10 to 200 % of the acid or acid anhydride added in the acid treatment.

9. Method according to any one of the preceding claims wherein in the hydration treatment the water content of the glyceride oil is 0.5 to 5 % by weight.

10. Glyceride oil refined according to the refining method of claim 1 to 9.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 0995

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 442 882 (SHOWA SANGYO CO., LTD) * Examples 1,2,4; page 4, lines 14-21; page 3, line 26 - page 4, line 9; page 5, lines 21-35; page 6, lines 4-32; page 7, lines 2-21; claims 1,3 * – – –	1-8	C 11 B 3/00
A	EP-A-0 269 277 (THE CAMBRIAN ENGINEERING GROUP LTD) * Page 3, lines 5-8,29-36,47; page 4, lines 3-24; examples 1-4; claims 1,3,4,8,11-14,17-25 * – – –	1-7,9	
A	GB-A-5 392 62 (THE SHARPLES CORP.) * Page 1, lines 80-98; page 2, lines 123-129; page 2, lines 34-49; page 4, lines 50-66; claims 1-3 * – – –	1,2,4, 8-10	
A	US-A-2 678 325 (J.A. CARLSON) * Column 1, lines 32-35; column 2, lines 27-39; column 3, lines 30-41; column 4, lines 19-21,30-39; claims 1,10,11 * – – –	1-4,6-8	
A	FR-A-2 303 849 (UNILEVER N.V.) * Page 3, lines 1-8; page 4, lines 12-13,19-22; page 5, lines 8-16; page 6, lines 6-15,21-24; examples 2,3,4-6,71; claims 1,4,8-14,19 * – – – – –	1-5,7,9, 10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 B

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	05 August 91	KANBIER D.T.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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