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54 Fat refining.

57 Fats especially for the preparation of cocoabutter substitutes are refined by contact in organic solution with an adsorption agent, preferably packed in a column down which the solution is percolated, the fat being pre-treated with bleaching earth of active carbon. This improves the life of the adsorbent which can be regenerated several times without loss of efficiency.

FAT REFININGTechnical Field

The field of the invention is the refining of fat, particularly but non-exclusively the refining of vegetable
5 butters.

From whatever source they are obtained, fats require purification in a refining process, to remove impurities and improve both the appearance and performance of the fat. In the edible context with which the invention is
10 concerned, taste also is improved by refining. The invention is particularly concerned with a class of fats known generally as vegetable butters from their relatively high melting characteristics, compared with the majority of fats from vegetable sources which are generally liquid at
15 ambient temperatures and are usually described as vegetable oils.

Oils and fats may be classified into two distinct groups differing markedly both in their properties and stability and require very different approaches in detail
20 to refining processes applied to them. Those high in polyunsaturation, including linoleic and more highly unsaturated fatty acids, and prized accordingly for their dietetic value, may contain 40% or more of these acids in their glycerides, they are liquid at ambient temperature

and are susceptible to the development of reversionary flavours after refining, owing to their susceptibility to oxidation arising from their high degree of unsaturation. Examples of these high PUFA vegetable oils include soyabean
5 containing 52% polyunsaturated fatty acids, cottonseed (53%), groundnut (32%), linseed (65% including no less than 53% of triunsaturated fatty acid), safflower (77%) and sunflower (64%). Marine oils are also notable for their high PUFA content.

10 In contrast, most animal fats are substantially less unsaturated. They are accordingly, high-melting and less prone to flavour reversion as are vegetable butters. Like most other vegetable fats, vegetable butters consist principally of triglycerides of predominantly C_{16} and
15 C_{18} fatty acids, but vegetable butters contain more saturated fatty acids. These are distributed principally in the alpha- or 1- and 3-positions of the triglycerides which constitute the principal component of fats and in this vegetable butters closely resemble cocobutter and in
20 their refined form are therefore used as cocoabutter substitutes since the close similarity of their structure is matched by similar melting performance including most importantly, organoleptic response. Examples of vegetable butters include cocobutter itself with only 4% linoleic
25 acid, shea (10%), sal (2.8%) mango kernel (5%) and mowrah (up to 18%), with palm oil (10%).

The application of selective adsorption methods for the removal on an industrial scale of impurities from glyceride oils and fats is a relatively recent event in
30 refinery practice. A miscella is made of the fat or oil in a suitable organic solvent, usually a hydrocarbon such as hexane, and the solution brought into contact with an appropriate adsorbent material of suitable particle size. The process necessitates removal of the solvent from the

raffinate solution and is therefore expensive to operate. The cost of the process may also be prohibitively high if the effective life of the adsorbent is short.

Nevertheless, the removal of the small quantities of polar
5 compounds present may have a dramatic effect, particularly on the melting characteristics of vegetable butters and is not readily achieved by alternative methods. The invention is particularly useful therefore in reducing the cost of achieving high quality fats for edible purposes such as
10 chocolate manufacture and also for pharmaceutical application by enhancing the effective life of adsorbents used for producing such fats.

Background art

USP 2,976,156 discloses a method of refining liquid
15 vegetable oils by contact with alumina adsorbent in which it is recommended that bleaching treatment can be omitted.

USP 3,955,004 discloses a similar process to that of USP 2,976,156 and in addition discloses as adsorbent mixtures of silica and alumina. The oils, which include
20 coconut, palm kernel and palm oil, are dissolved in a suitable solvent. After contact with the adsorbent, the refined oil is separated from the solvent and bleached.

French Patent 990704 discloses bleaching a solution of glyceride oil and subjecting the solution to silica
25 treatment. None of these references reveals the necessity for combining the application of adsorption and bleaching steps with regeneration as provided for by the present invention and applied to vegetable butters to be fractionated.

USP 4,284,580 describes the fractionation of triglyceride mixtures by selective adsorption on surface-aluminated silica gel adsorbent. The process disclosed in this reference relies upon differential adsorption characteristics exhibited by different degrees of unsaturation between the many triglycerides of glyceride oils and fats in order to obtain fractions of different Iodine Values.

Indian Oil Soap Journal (1969), 34 (7), pages 147-150. Laboratory scale purification of sal oil is described in which crude sal oil is purified by chromatography in benzene solution over an alumina column. No column regeneration is described, nor was the solution pre-bleached.

USP 2,589,097 describes the removal of reversionary flavours from soyabean and similar highly unsaturated oils, which may first be bleached, using column adsorption treatment.

European Patent Application 53016 published 2nd June 1982 describes refining sal fat by contact with a specially prepared particulate adsorbent in a column.

General description of the invention

This invention relates to fat refining, particularly but not exclusively to refining vegetable butters.

Fats may be refined by contact, in a solution or miscella of a non-polar solvent, with an adsorption agent, usually packed in a column and based on silica and/or alumina activated by heat treatment. The adsorption agent selectively retains polar impurities, for example partial

glycerides and colouring matter, and oxidised compounds which are highly polar, whereas the triglycerides constituting the principal components of the fats remain unabsorbed in a raffinate from which the purified fat is
5 recovered by removing the solvent.

The absorption agents become less effective with prolonged and/or repeated use, as polar compounds accumulate on them. Desorption of these polar compounds by treatment with polar solvents is incompletely effective
10 with the more tenacious polar compounds absorbed from vegetable butters such as shea, sal and others. We have now found that regeneration is facilitated by subjecting the fat or the fat miscella to pretreatment by contact with bleaching earth and/or active carbon, to adsorb the more
15 highly polar compounds before treatment with the adsorption agent, preferably packed in a column through which the miscella is percolated. The less highly polar compounds, e.g. diglycerides, adsorbed by the adsorption agent may then be readily removed in a subsequent desorption step,
20 e.g. by percolation with a polar solvent. The refined fat may be separated from the raffinate, for example by distilling off the non-polar solvent, or by fractional crystallisation, preferably to recover a fat fraction having a slip melting point of at least 35°C.

25 Excepting the lauric fats, e.g. palm kernel and coconut oil, about $\frac{1}{3}$ of the triglycerides of the fats with which the invention is chiefly concerned are symmetrical, disaturated C₁₆/C₁₈ triglycerides. Generally they contain less than 20% linoleic acid and, for
30 the most part, not more than 10% and are low in polyunsaturated fatty acids generally.

Such fats are usually expelled or extracted from tropical or sub-tropical fruit, either the fruit seeds or

whole fruit. Although sometimes cultivated in plantations, as for palm oil, usually the fruit grows wild and is collected at irregular intervals in the forests after having fallen. Due to the prevailing elevated temperature and the moisture content of the earth, extensive enzymic reaction can occur, converting the natural triglycerides of the fats contained in the fruit seeds or in the pericarp by hydrolysis to mono- and diglycerides and free fatty acids. Other common reactions encountered in the fruit are hydroperoxidation, epoxidation and hydroxylation of the unsaturated fatty acid radicals contained in the triglycerides of the fat. These enzymic reactions produce a host of highly polar compounds which adhere tenaciously onto adsorbents, both on their surface and in their pores, which makes their desorption very difficult and which consequently result in the failure to regenerate the adsorbents for re-use.

The solvent in the fat miscella is preferably hexane or other inert aliphatic hydrocarbon compositions, preferably with a boiling point below 100°C to facilitate evaporation from the miscella without exposing the fat to excessively high temperatures. The fat in the miscella may be in crude form or undergo some preliminary refining beforehand, preferably neutralisation.

Regeneration comprises desorption and reactivation, preferably effected in two steps. In the first step adsorbed polar compounds are desorbed from the adsorbents by contact with a polar organic solvent which preferably comprises a monohydric fatty alcohol containing up to 6 carbon atoms and particularly methanol, ethanol and isopropanol, and alcohol-hydrocarbon mixtures, preferably aliphatic, which may be miscible or immiscible, preferably azeotropic mixtures to facilitate removal from the regenerated adsorbent by evaporation. In the second step,

residual polar solvent (e.g. methanol) used for the desorption operation is driven out of the column by heating and preferably a volatile aliphatic hydrocarbon, e.g. hexane either in the vapour phase or as a superheated liquid. The formation of azeotropic mixtures is also helpful in this case. Herein the first step is called "desorption" and the second step "reactivation".

Pretreatment, adsorption and desorption are preferably carried out at temperatures from 15 to 75°C, more preferably not in excess of 60°C, but pretreatment in particular may be carried out at temperatures from 30 to 110°C and adsorption and desorption at 40 to 80°C. Adsorption is preferably effected in particular at 30 to 60°C, particularly approximately between 20 and 50%.

Reactivation is preferably carried out between 50 to 170°C. Substantially less bleaching aid or active carbon is used in the pre-treatment step than adsorption agent, from 0.5 to 5% by weight of the fat being adequate for the former, but with preferably a fat:adsorbent ratio from 10:1 to 1:1 by weight of the fat. Preferably both the pre-treatment and adsorption steps are applied to the same solution of fat.

Suitable bleaching earths for use in the invention include activated Fuller's earth, for example Tonsil and Fulmont, Lucilite, Kieselsäure of Degussa. Granulated or non-granulated active carbon, e.g. Norit, may alternatively or in addition be used. Bleaching earths are usually acid-activated natural earths of structures typified by Montmorillonit and Bentonit. Acid treatment increases their propensity for adsorption of highly polar organic compounds including highly polar pigments, e.g. chlorophyll. These earths are not suitable for the adsorption of bulk amounts of diglycerides etc, but very

useful in the preliminary treatment step for the removal of small amounts of highly polar organic compounds prior to the treatment of the fat with adsorbents like silica gel or Al_2O_3 . These highly polar compounds otherwise prevent the regeneration of the adsorbents like silica gel and make their reuse difficult, if not impossible.

Active carbon also adsorbs highly polar compounds both by surface adsorption (e.g. pigments etc) and also by π -electron interaction (e.g. aromatic compounds, polyene compounds, etc). All active carbons, both granulated and non-granulated, are suitable for this purpose and may be used in conjunction with bleaching earths.

The adsorption agent may comprise silica gel, alumina or mixtures thereof including co-precipitates. Examples of aluminas include gibbsite and bayerite and among proprietary examples include Aluminiumoxid 504C. Suitable silica gels include Sorbsil of Messrs J Crosfield & Sons Limited, Warrington, England and Kieselgel-M of Messrs Herrmann, Cologne, Germany.

Preferably adsorption is effected by percolating the miscella through a column packed with the adsorbent and with a length:diameter ratio of 5:1 to 1:2, particularly approximately equal diameter and length, with a residence time in the column of 5 to 30 minutes, especially 15 to 25 minutes.

Adsorbents suitable for use in the process of the invention preferably exhibit a specific surface area of 300 to 500 m^2/g , a pore volume of 0.7 to 1.5 mls/g , an average pore diameter of 30 to 2000 Å, preferably 60 to 180 Å, a weight:volume ratio of 0.2:0.5 g/ml and pH of 6.5 to 7.5. Preferably silica gel adsorbent used in this invention contains more than 95% SiO_2 with not more than

approximately 4 to 8% of volatiles removed at 140°C after 4 hours. Particle size by sieve analysis should preferably include not more than approximately 5% of 0.3 mm and not more than 25% of 0.2 mm.

5

EXAMPLE 1

40 g of the neutralised solid fraction (0.1% free fatty acids) remaining from dry fractionating crude sal fat obtained by solvent extraction of the seeds of sal fruits (*Shorea robusta*) were dissolved to form a 20% solution in 10 hexane which was pretreated with 2% bleaching earth Tonsil ACCFF and 0.4% active carbon Norit FND at 25 to 40°C with agitation for 45 minutes before the bleaching earth and the carbon was filtered off and the pretreated hexane solution passed at 40°C down a column 3 cm in diameter and 21 cm 15 long, packed with silica gel (Kieselgel M of Messrs Herrmann, Cologne), using a residence time of 12 minutes and a fat:gel ratio of 2:1. After collecting the eluate raffinate the silica was regenerated by washing in the column with isopropanol/hexane 20/80 mixture, removed 20 from the column and dried at 160°C for 16 hours and reused as before, adopting the same quantity of fat each cycle. Particulars of the gel are as follows:- Specific surface area 450 m²/g, pore volume 0.73 mls/g, average pore diameter 60Å weight:volume ratio 0.43 g/ml, pH 7.2, 25 SiO₂ 99.0%, volatiles as above 2.4%, sieve analysis 2% of 0.2 mm, 75% of 0.1 mm, 18% of 0.063 mm and 4.5% of 0.05 mm and 0.5% of 0.04 mm.

5 cycles were completed and the fat recovered from the eluate raffinate and examined after each upon removing 30 the solvent.

The same fat and the same gel was used for a similar series of experiments in which the miscella pretreatment

with bleaching earth and active carbon was omitted. After 5 regeneration cycles the eluate fats and the used silica gels were compared with each other.

Results appear in the accompanying Table 1, in which 5 the Lovibond measurements were made in a 1" cell for the crude fat and a 2" cell for the treated samples.

The results show that the silica-treated raffinates which are miscella-bleached prior to silica treatment, remain consistently high in quality, even after several 10 recycles, whereas those without previous miscella-bleaching show progressive deterioration in properties with increasing recycling of the silica. This is also reflected in the colour measurement of the silicas after the 6th regeneration. The sample used for treating the 15 miscella-bleached samples showed a lighter colour (yellow index 27.3 as measured by Zeiss Elrepho instrument) than the corresponding sample used for treating the fat without previous miscella-bleaching (yellow index 42.6).

TABLE 1

Factor	Crude fat wt %	Raffinate (with miscella pretreatment)						Raffinate (without miscella pretreatment)					
		Regenerated SiO ₂					Fresh SiO ₂	Regenerated SiO ₂					Fresh SiO ₂
		1.run	2.run	3.run	4.run	5.run	6.run	1.run	2.run	3.run	4.run	5.run	6.run
Diglyceride	4.4 wt %	0.1%	0.1%	0.2%	0.3%	0.3%	0.3%	0.1%	0.5%	0.7%	0.9%	1.0%	1.1%
Dihydroxy triglyceride	2.9%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.2	0.2
Loyibond at 40°C	70 Y+ 10 R+ 14 B	30 Y+ 0.1R	30 Y+ 0.5R	30 Y+ 0.5R	40 Y+ 0.8R	40 Y+ 0.8R	40 Y+ 0.8R	40 Y+ 2.0R	60 Y+ 2.0R	60 Y+ 2.0R	70 Y+ 3.5R	70 Y+ 3.5R	70 Y+ 3.8R +0.9B

EXAMPLE 2

A solution in hexane of neutral illipé fat was pre-treated with bleaching earth and carbon as described in Example 1 and passed down a column 0.85 m in diameter, 5 packed to a depth of 0.85 m with silica gel of the type "Sorbsil" from Messrs J Crosfield & Sons Ltd, Warrington, England, the weight of silica gel being the same weight as the fat. The gel characteristics were as follows:
Total surface = $331 \text{ m}^2/\text{g}$, pore volume = 1.16 ml/g , pore
10 diameter = $140 \text{ \AA}$, pH = 7.6, weight:volume ratio = 0.35 g/ml , SiO_2 content = 99.1%, particle size = 85.5% between 0.05 and 0.2 mm, 5.5% above 0.3 mm and 9% below 0.05 mm.

After distilling off the hexane a light-coloured refined fat practically free of diglycerides was obtained
15 from the refined solution.

The spent silica column was then washed down at 80°C under pressure with an azeotrope mixture of isopropanol and hexane in a weight ratio of 22:78, to desorb and remove the material adsorbed on the silica. The column was then
20 reactivated for reuse by passing down hexane at 180°C and 13-bar. The reactivated silica column was used again to refine a fresh batch of neutralised illipé, pre-treated as described, the whole cycle of refining, desorption and reactivation being repeated 15 times.

25 Neutralised illipé from the same batch was similarly refined by treatment with silica but without the pre-treatment. The silica progressively lost its adsorptive capacity with repeated reuse. This was shown by the increasing diglyceride content of the refined fat and
30 its increasing colour and also by the considerable drop in stabilised dilatation values D of the fat at 32.5°C . These results are shown in Table 2 and clearly demonstrate that

the miscella pre-treatment purifies the neutralised fat to such an extent that after subsequent silica treatment the spent silica can be regenerated successfully by desorbing with a mixture of isopropanol and hexane and reactivated by 5 superheated hexane. Such a regenerated silica gel can be reused for satisfactory diglyceride removal from the illipé fat. Omission of the pre-treatment eventually renders the spent silica non-regenerable, as evidenced by total failure to adsorb diglycerides after limited reuse.

TABLE 2

Oil	Control						Pretreated					
	Y	R	B	di %	D		Y	R	B	di %	D	
Run												
Crude	70	25	7	15.6	395							
1 Fresh silica	10	0.3	0	0.2	1200							
5	1.5	0.7	0	1.8	1215		10	0	0	0.4	1150	
4	20	1.8	0	3.8	1200		10	0.5	0	0.9	790	
7	40	6	1.5	6.4	1240		10	0.6	0	1.0	540	
10	70	8	5	9.0	1210		10	0.7	0	1.8	450	
15	70	20	7	15.6	1200		10	0.7	0	2.1	400	

EXAMPLE 3

A solution of neutralised shea nut fat in twice its weight of hexane, was bleached at 80°C with 2% bleaching earth "Tonsil ACCFF" from Messrs Südchemie, Munich, Germany. The filtered solution was passed through a column as before, but packed with silica "Kieselgel M" from Messrs Herrmann, Cologne, Germany, using half as much gel as fat by weight and a refined fat recovered by evaporating the solvent from the treated solutions.

10 The spent silica was desorbed in the column by washing with a mixture of 85 vol % hexane and 15 vol % methanol at 50°C and reactivated by passing hexane vapour under pressure at 90°C inlet temperature through the column, until methanol was completely driven out. The
15 column was reactivated and reused 5 times, the diglyceride content being determined of the fat recovered after each use.

In a control test the unbleached neutralised fat was similarly refined and the diglyceride content of the
20 refined fat compared as shown in Table 3, from which it is evident that bleaching prior to silica treatment exercises a beneficial effect on regeneration and reuse of the silica.

Table 3

Diglyceride content	crude fat	Raffinate (with prebleached fat)						Raffinate (without prebleaching)					
		Fresh SiO ₂						Regenerated SiO ₂					
		1.run	2.run	3.run	4.run	5.run	6.run	1.run	2.run	3.run	4.run	5.run	6.run
	11.2 %	0.1 %	0.2 %	0.2 %	0.3 %	0.2 %	0.2 %	0.1 %	0.5 %	1.2 %	2.6 %	4.4 %	6.8 %

CLAIMS

1. Process for refining glyceride fats by contact with adsorbent material to remove polar impurities by selective adsorption, wherein the fat is first contacted with bleaching earth or active carbon and then in organic solution with a particulate adsorbent and refined fat recovered from the raffinate solution and separated therefrom.
2. Process according to Claim 1, in which the fat comprises a vegetable fat low in polyunsaturated fatty acids.
3. Process according to Claim 2, in which the fat is shea, sal, illipé, mango kernel, aceituno, palm, olive oil or fractions or mixtures thereof.
4. Process according to any of the preceding claims, wherein the refined fat is fractionated by fractional crystallisation to recover a fraction having a slip melting point of at least 35°C.
5. Process according to any of the preceding claims, wherein the solvent is an aliphatic hydrocarbon.
6. Process according to Claim 5, wherein the solvent comprises hexane.
7. Process according to any of the preceding claims, wherein the adsorbent is periodically regenerated.
8. Process according to Claim 7, wherein the regeneration comprises desorption and reactivation steps, wherein the adsorbent is first contacted with a polar organic solvent and subsequently heated to remove residual solvent.

9. Process according to Claim 8, in which adsorption and desorption are effected at 40 to 80°C.
10. Process according to Claim 8 or 9, in which reactivation is effected at 60 to 170°C.
11. Process according to any of the preceding claims, in which the fat:adsorbent ratio is 1:1 to 10:1 by weight of the fat.
12. Process according to any of the preceding claims, in which from 0.5 to 5% of bleach or active carbon is used by weight of fat.
13. Process according to any of the preceding claims, wherein the bleach comprises Fullers' Earth.
14. Process according to any of the preceding claims, wherein the adsorbent comprises silica gel, alumina, or their mixtures or coprecipitates.
15. Process according to any of the preceding claims, wherein the adsorbent is packed in a column with a length:diameter ratio of 5:1 to 1:2.
16. Process according to any of the preceding claims, wherein the residence time of the adsorbent is from 5 to 30 minutes.
17. Process according to any of the preceding claims, wherein the adsorbent exhibits a specific surface area of 300 to 500 m²/g, a pore volume of 0.7 to 1.5 mls/g, an average pore diameter of 30 to 2,000Å and a weight:volume ratio of 0.3:0.5 gms/ml.

18. Process according to any of the preceding claims, wherein the particle size of the adsorbent includes not more than about 5% of 0.3 mls and not more than 25% of 0.2 mls.

19. Process according to any of the preceding Claims 7 to 18, wherein the adsorbent is regenerated by contact with an azeotrope.

20. Process according to Claim 1 substantially as hereinafter described with reference to the accompanying Examples.

21. Fats whenever refined by a process as claimed in any of the preceding claims.



European Patent
Office

EUROPEAN SEARCH REPORT

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Application number

EP 82 30 6102

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. 3)
X,Y	--- CHEMICAL ABSTRACTS, vol. 71, no. 12, 22nd September 1969, page 95, no. 51473e, Columbus Ohio (USA); C.SHRINIVASULU et al.: "Salseed, Shorea robusta. I." & INDIAN OIL SOAP J. (CAT. D) 1969, 34(7), 147-50. *Abstract*	1,2,3, 5,6,7, 8,13, 14,19, 20,21	C 11 B 3/10
Y	--- US-A-2 573 509 (R.J.TAYLOR) *Claims 1,7*	1,7,8, 19	
X	--- FR-A-2 241 613 (UNILEVER) *Claims 1,3,4,5; page 2, lines 20-26,35-39; page 3, lines 15-24; page 4, lines 1-13,31-33*	1,2,3, 5,6,11 -14,17 ,20,21	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 11 B

The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-02-1983	Examiner PEETERS J.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	