

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of Refining Vegetable and Animal Oils

We, MARCHON PRODUCTS LIMITED, a British Company, of 140 Park Lane, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an improved method of refining vegetable and animal oils.

The conventional method of refining crude oils when an edible product is required involves treating the crude oil with an aqueous alkaline solution, such as dilute sodium hydroxide or sodium carbonate, followed by several water washes and, if necessary, by an adsorptive bleaching process using activated earths; in some cases, a process of deodorisation is used which consists of blowing steam or inert gas through the oil at an elevated temperature and in vacuum.

In the alkali refining process, free fatty acids present in the crude oil are removed as soaps and the inherent disadvantage of this method of refining lies in the fact that the soap forms a micella solution in water which solvates appreciable quantities of the glyceride oil. Thus not only is there a loss of the glyceride oil but also the fatty acids recovered from the refining process (acid oils) are contaminated with larger or smaller amounts of glyceride oil.

It has been proposed to use soaps of certain fatty acids such as sodium resinate, sodium oleate and free organic acids such as salicylic acid and naphthenic acids as aids in the refining of glyceride oils. These compounds fall within the group known as hydrotropes. In this case the aqueous medium behaves more like a true solution and does not solvate glyceride oil, or does so only to a small extent. Thus only small quantities of the glyceride oils are carried into the aqueous phase by the treating solution. However, during the recovery of the oil-derived fatty acid from the soap layer by acidification thereof with

a strong mineral acid, usually sulphuric acid, the hydrotropes present react with the mineral acid to yield free organic acids or decomposition products. These reaction products usually remain in the fatty acid product as contaminants.

We have now found that if urea or the alkali-, or alkaline earth-metal salts of aryl- and alkaryl-sulphonic acids are used as the hydrotropes, the contamination of the fatty acid product is substantially avoided.

Accordingly, the invention consists in a method of refining vegetable and animal oils which comprises mixing the oil at an elevated temperature with a dilute aqueous solution of an alkali, together with urea or an alkali metal, or alkaline earth metal, salt of an aryl or alkaryl sulphonic acid as hydrotrope, allowing the mixture to separate into an aqueous soap layer and an oily layer and removing the aqueous layer.

Besides fatty acids, other polar bodies such as proteins, aldehydes and colouring matter which are more hydrophilic than the glyceride oils but somewhat less hydrophilic than the soaps, are also removed from the oil phase into the aqueous phase. Because of this the oils obtained by our method are substantially equal in quality to oils obtained by conventional refining methods which involve purification in several stages including alkali refining, adsorptive bleaching and de-odorising. By using our method it may be possible in some cases to reduce the number of refining stages to one.

If an even higher degree of purity is required the oil layer, after separation of the soap/hydrotrope mixture, may be treated with a further small quantity of hydrotrope in aqueous solution and the two layers formed allowed to separate. The aqueous layer is separated off and the oil layer, after a wash with water, is dried under vacuum to obtain substantially pure glyceride oil.

The hydrotropes for present use are defined

[Price 4s. 6d.]

as being urea, and the alkali metal and alkaline earth metal salts of those aryl and alkyl-aryl sulphonic acids which do not markedly depress the surface tension of water, that is, those in which any alkyl groups present do not contain more than 8 carbon atoms. Examples of such compounds include the sodium or potassium benzene, toluene, cymene and xylene sulphonates, especially those sold by the Applicants under the registered Trade Mark ELTESOL SX. The sodium salts of the benzene or alkyl benzene sulphonic acids, such as sodium xylene sulphonate or sodium toluene sulphonate, which is sold under the Registered Trade Name ELTESOL ST, are particularly economic.

An advantage of our process is that it can be used for purifying crude oils which contain more than the normal amount of fatty acids and which would not be worth refining or even impossible to refine by conventional methods owing to the excessive loss of oil or by the impossibility of breaking the soap/oil emulsions. In particular, tallow oils, which contain as much as 25% fatty acids, can be refined by the method of our invention with very little loss of glyceride oil.

The concentration of the alkali solution used and the temperature at which the separation is carried out may be substantially the same as in the conventional method of refining, a 20% sodium hydroxide solution being usually found satisfactory and a temperature as low as is compatible with the melting point and viscosity of the oil. The amount of hydrotrope required depends on the acid value of the oil. A suitable amount

of hydrotrope can readily be established for each oil by simple treatment, but as a rough guide each unit of acid value in the crude oil requires from 1 to 3% of 100% hydrotrope. The proportion of hydrotrope to water may advantageously be about 40-60% by weight.

The aqueous layer obtained by treatment of the oil with alkali and hydrotrope (or the combined aqueous layers where there has been more than one treatment with hydrotrope) may be treated with a mineral acid, preferably sulphuric acid, to recover its fatty acid content. After acidification, the mixture is allowed to settle and two layers are formed. The top layer consists of the fatty acids. The aqueous layer may be worked up to recover the hydrotrope. The sodium salts of alkyl benzene sulphonic acids lend themselves especially readily to recovery and re-use since, in the recovery of the fatty acids by acidification with sulphuric acid, the solubility of the sodium sulphate formed is markedly decreased by the presence of the alkyl benzene sulphonic acid salt. Consequently, after removal of the fatty acid, sodium sulphate can be readily crystallised at temperatures below 30°C as the deca-hydrate and, after filtration, the hydrotrope solution can be recycled to the process directly or, if desired, after a certain amount of concentration. Small amounts of sodium sulphate do not interfere with the refining process. The effect of sodium xylene sulphonate (S.X.S.) on the solubility of sodium sulphate at 16°C is illustrated in the table below.

	H ₂ O%	S.X.S. %	Na ₂ SO ₄ %
Mixture	46	50	4
Filtrate	48.7	50.2	1.1
Mixture	63	30	7
Filtrate	62.8	35.3	1.9
Mixture	80	10	10
Filtrate	84.0	12.5	3.5

The fatty acid mixture obtained by acidification of the aqueous layer derived from the original alkali treatment is generally contaminated with glyceride oil and has a low commercial value. According to a feature of the invention the process for recovering the fatty acids just described is modified so as to give a fatty acid of improved purity. The aqueous layer derived from the original alkali treatment is boiled with at least sufficient alkali to hydrolyse the glyceride oil to give a further quantity of fatty acid soap and glycerol, the mixture is acidified with a mine-

ral acid to hydrolyse the soap, the resulting mixture is allowed to form two layers, and the lower, aqueous layer is removed to leave a fatty acid layer of improved purity. It will be understood that the aqueous layer used as starting material for this process contains the hydrotrope originally used. The presence of a hydrotrope is essential to the success of the process since without it, boiling of the mixture would be a difficult or impossible task owing to foaming caused by the soap, this foaming being wholly or largely prevented by the hydrotrope. All the alkali necessary for

the process of the invention may be provided by adding a sufficient excess of alkali in the original treatment of the raw glyceride oil. Alternatively some or all of the alkali may be provided separately after this initial refining process.

In carrying out the process just described, the original oil and acid mixture may first be treated as before, but with approximately twice the amount of alkali required to saponify the acids present, in the presence of a hydrotrope. The resulting mixture separates into an upper purified oil layer and a lower aqueous layer, which contains the saponified acids, hydrotrope, excess alkali and some entrained glyceride oil. This aqueous layer is run off and boiled for about one hour. At this temperature and time the alkali present splits the glyceride oil. If necessary, further alkali may be added at this stage in order to give an excess calculated on the glyceride which is present. The presence of the hydrotrope at this stage is essential, since it prevents the boiling soap solution from frothing.

The soap solution is now acidified to liberate the fatty acids, and the resulting mixture allowed to separate into two layers, an upper fatty acid layer of improved purity and a lower aqueous layer, which is run off. The aqueous layer contains hydrotrope, the sodium salt of the mineral acid, which is preferably sulphuric, added to liberate the fatty acids from the soap solution, and glycerol which is produced with fatty acids when the glyceride oil is split by the alkali. This aqueous layer is treated as described above to recover the hydrotrope solution, which is recycled. Hence, the process as a whole lends itself to continuous operation. It should be noted, however, that the recycled hydrotrope solution will gradually accumulate impurities, mainly glycerol and the residual amount of sodium sulphate. After a time these impuri-

ties will adversely affect the process. When this occurs, the solution may be discarded or put through an ion-inclusion column to remove the glycerol whereupon the purified hydrotrope solution may then be recycled.

Where the original glyceride oil contains phosphatides, e.g. in the case of soya bean oil, we have found that these are extracted into the aqueous hydrotrope layer and can be recovered therefrom by known methods. The phosphatides, e.g. lecithin, may be valuable by-products of the process.

The following Examples serve to illustrate the invention, all parts being by weight: The term saponification value is used to indicate that amount of KOH required to neutralise the fatty acid and to saponify any oil therein. Both saponification and acid values are given in terms of mgKOH/g.

EXAMPLE 1

200 parts of good colour tallow oil (acid value 2.7 mg KOH/g) were heated to 95°C. To the hot oil was added 10 parts of sodium xylene sulphonate (SXS) as a 60% solution in water. Caustic soda (10% excess based on the acid value) was then added as a 20% solution. The mixture was stirred and then allowed to settle. After separating the aqueous layer, the oil was washed a second time with 30% SXS, separated, washed with water and then dried under vacuum at a temperature of 95°C. The combined aqueous layers were treated with sulphuric acid to liberate the fatty acids. After removal of the fatty acids, the sodium sulphate was crystallised out and filtered off to give a solution of SXS for re-use.

The above treatment was repeated using 14 parts and 20 parts of SXS respectively. The results of all three treatments are shown in Table 1. Also included in the table are the results obtained when the treatment was carried out without the use of a hydrotrope.

TABLE I

Good Colour Tallow. Acid Value 2.7
Saponification Value 196

%SXS BASED ON OIL	RECOVERED FATTY ACIDS				NEUTRAL OIL
	WEIGHT PARTS	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
5	2.8	194	206	0.085	0.1
7	2.5	195	203	0.05	0.1
10	2.75	197	206	0.06	0.05
nil	2.77	135	212	0.54	0.25

EXAMPLE 2.

A similar separation was carried out as described in Example 1 using 200 parts of

medium colour tallow oil. The results are shown in Table II.

TABLE II

Medium Colour Tallow.				Acid Value	26.7
				Saponification Value	197.5
RECOVERED FATTY ACIDS					NEUTRAL OIL
% SXS BASED ON OIL	WEIGHT PARTS	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
28	26.9	181	206	1.7	0.15
nil	UNREFINABLE				

Part of the aqueous layer containing 1.7% glyceride oil, was heated to boiling for 1 hour with 10% excess alkali on the glyceride oil. On acidification with sulphuric acid, the solution separated into two layers and the lower, aqueous layer was removed to leave a fatty acid layer with the following analysis.

Acid Value 207
Saponification Value 207

EXAMPLE 3.

A similar separation was carried out as described in Example 1 using 200 parts of soya bean oil. The results are shown in Table III.

TABLE III

Soya Bean Oil				Acid Value	2.9
				Saponification Value	194.0
RECOVERED FATTY ACIDS					NEUTRAL OIL
% SXS BASED ON OIL	WEIGHT PARTS	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
6	1.69	175	206	0.13	0.05
nil	3.51	104	206.8	0.45	0.38

- 20 Part of the aqueous layer containing 0.13% glyceride oil was heated to boiling for 1 hour without any further addition of alkali. On acidification with sulphuric acid, the solution separated into two layers, and the lower, aqueous layer was removed to leave a fatty acid layer with the following analysis.
- 25

Acid value 206
Saponification Value 206

EXAMPLE 4.

A similar separation was carried out as described in Example 1 using 200 parts of maize oil. The results are shown in Table IV.

TABLE IV

Maize Oil		Acid Value		6.4	
		Saponification Value		193.4	
RECOVERED FATTY ACIDS				NEUTRAL OIL	
% SXS BASED ON OIL	WEIGHT PARTS	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
10	5.62	181.2	208	0.39	0.15
nil	7.94	115.6	206.5	1.87	0.34

One method of extracting vegetable oils is to digest crushed seeds with a hydrocarbon solvent, for example hexane. We have found that the resulting solution of the oil is excellently suited to the process of the invention since the separation into the aqueous hydro-trope/soap layer and the oil/solvent layer is much quicker than is the case when the oil undissolved in hydrocarbon is used. For example where undissolved oil is used, the separation may take a matter of hours, but where the solution in hexane is used, the separation may take 2 or 3 minutes. It is understood that in the description of the invention and the claims herein, the term "oil" includes, where the context permits, solutions of oil in hydrocarbon solvents.

In view of the short time required for sepa-

ration of the aqueous and solvent phases, the use of hydrocarbon solutions of the oils lends itself with especial advantage to the operation of the invention as a continuous process.

EXAMPLE 5.

A separation was carried out as described in Example 1 using solutions of soya bean oil with an acid value of 1.12 and saponification value of 191 in hexane as follows:

(a) Solution of 91.4g oil in 300 ml hexane.

(b) Solution of 217g oil in 250 ml hexane.

After stirring of the mixture of oil, solvent, hydrotrope, alkali and water, separation into two layers took place in approximately 2 minutes. The results of the process are shown in Table V.

TABLE V

RECOVERED FATTY ACIDS				NEUTRAL OIL	
% SXS BASED ON OIL	WEIGHT g	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
(a) 6.5	0.52	131	198	0.18	0.065
(b) 50	1.63	110	199	0.33	0.04

WHAT WE CLAIM IS:—

1. A method of refining vegetable and animal oils which comprises mixing the oil at an elevated temperature with a dilute aqueous solution of an alkali, together with urea or an alkali metal or alkaline earth metal, salt of an aryl or alkyl-aryl sulphonic acid as hydrotrope, allowing the mixture to separate into an aqueous soap layer and an oily layer and removing the aqueous layer.

2. A method as claimed in Claim 1 wherein

the hydrotrope is an alkali metal or alkaline earth metal salt of an alkyl aryl sulphonic acid in which each alkyl group does not contain more than 8 carbon atoms.

3. A method as claimed in Claim 2, wherein the hydrotrope is an alkali metal salt of xylene or toluene sulphonic acid.

4. A method as claimed in any of the preceding claims, wherein the amount of hydrotrope present is 1 to 3% of the weight of the oil for every unit of acid value of



TABLE IV

Maize Oil			Acid Value		6.4
			Saponification Value		193.4
RECOVERED FATTY ACIDS					NEUTRAL OIL
% SXS BASED ON OIL	WEIGHT PARTS	ACID VALUE	SAPONIFI- CATION VALUE	% NEUTRAL OIL ENTRAINED	ACID VALUE
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nil	7.94	115.6	206.5	1.87	0.34

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RECOVERED FATTY ACIDS				NEUTRAL OIL	
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2. A method as claimed in Claim 1 wherein

the hydrotrope is an alkali metal or alkaline earth metal salt of an alkyl aryl sulphonic acid in which each alkyl group does not contain more than 8 carbon atoms.

3. A method as claimed in Claim 2, wherein the hydrotrope is an alkali metal salt of xylene or toluene sulphonic acid.

4. A method as claimed in any of the preceding claims, wherein the amount of hydrotrope present is 1 to 3% of the weight of the oil for every unit of acid value of



the crude oil.

- 5 5. A method as claimed in any of the preceding claims, wherein the proportion of hydrotrope to water is from 40 to 60% by weight.

- 10 6. A method as claimed in any of the preceding claims, wherein the oily layer, after removal of the aqueous layer, is treated with a further quantity of the hydrotrope in aqueous solution.

- 15 7. A method as claimed in any of the preceding claims, wherein the aqueous soap layer or combined aqueous soap layers is or are acidified with a mineral acid, the mixture is allowed to separate into a fatty acid layer and an aqueous hydrotrope layer and the aqueous hydrotrope layer is withdrawn.

- 20 8. A method as claimed in Claim 7, wherein the mineral acid salt present in the aqueous hydrotrope layer is crystallised out and removed, and the filtrate is recycled.

- 25 9. A modification of the method as claimed in claim 7 and 8, wherein, before acidification, the said aqueous soap layer is boiled with at least sufficient alkali to hydrolyse any gly-

ceride oil present to give a further quantity of fatty acid soap and glycerol, and the mixture is then acidified with a mineral acid to hydrolyse the soap, the resulting mixture is allowed to form two layers, and the lower, aqueous layer is removed to leave a fatty acid layer of improved purity.

- 30 10. A method as claimed in any of the preceding claims, wherein the crude oil contains phosphatides which are extracted into the aqueous layer and the phosphatides are recovered from the said layer by conventional methods.

- 35 11. A method of refining vegetable and animal oils, substantially as described in any of the Examples herein.

- 40 12. Vegetable and animal oils and fatty acids whenever prepared by a method as claimed in any of the preceding claims.

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