

PATENT SPECIFICATION

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- (21) Application No. 40053/74 (22) Filed 13 Sept. 1974
(31) Convention Application No. 48/104 258
(32) Filed 14 Sept. 1973 in
(33) Japan (JA)
(44) Complete Specification published 2 Nov. 1977
(51) INT CL² C11B 3/06
(52) Index at acceptance C5C 5A3 5A4 5B2



(54) METHOD OF FRACTIONATING OILS AND FATS

(71) We, FUJI OIL COMPANY, LIMITED, a Corporation of Japan, residing at No. 6—1 Hachiman-cho, Minami-ku, Osaka-shi, Japan, 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:—

This invention relates to a fractionation of oils and fats (hereinafter referred to as "oils"), and more particularly but not exclusively provides a method suitable for use on an industrial scale for the separation of oils into a higher melting portion (which is usually solid at room temperature) and a lower melting portion (which is usually a liquid at room temperature).

Heretofore, there have been proposed many methods for separating oils into two or more different melting portions. The most typical one is fractionation by solvent and the second is winterizing. The former is suitable for precise fractionation, but it uses expensive and dangerous solvents. Winterizing is simple and does not require any solvent, but in this method the separation of the higher melting portion from the lower melting portion is usually incomplete because of the high viscosity of the former.

An improvement in the ordinary winterizing method is described in Japanese Patent No. 230,155 (to which British Patent Specification No. 743,166 corresponds). In this method a mixture of surfactant, such as an alkyl benzene sulphonate, an alkyl sulphonate or a fatty alcohol sulphate and water (and further with or without sodium or magnesium sulphate) is used for making a polyphase suspension wherein the crystalline solid portion (the higher melting portion) and the liquid portion (the lower melting portion) are suspended in the solution of the surfactant. In principle, the surfactant induces a lowering of the interfacial tension between both the solid and liquid portions which effects a decrease in the viscosity of the suspension which permits a good separation. The fractionation of this prior method is almost satisfactory; however, the surfactant such as an alkyl benzene sulphonate or an alkyl sulphonate which is particularly useful in this process is too stable to be degraded by the natural clarifying actions and further it is more or less poisonous to all living creatures even to bacteria. Consequently, if an enormous amount of said surfactant is discarded from such fractionation, it may become a serious environmental hazard. Further, such surfactant has vigorous foaming action which cause troublesome blocks in sewer-pipes.

To prevent or to minimize public nuisance is now a major problem for industry and this situation in the fractionation of oils has not changed in the past decade. For example, recent Japanese Patent Publication No. 35,272/71 describes the use of sodium decyl sulphate as the surfactant. We are not aware that in the oil industry a process has been operated which provides a satisfactory minimum effluent problem. To exclude pollution or effluent problems entirely when using ordinary surfactants involves vast expense. Thus, at present, the fractionation of oils by the surfactant process has, in fact, been forced to greatly minimise or almost cease in many oil factories.

The present invention provides a method of fractionating oils and fats which method comprises contacting a suspension of a solid higher melting fraction of an oil or fat in a liquid lower-melting fraction, the oil or fat containing free fatty acids with an aqueous solution comprising an electrolyte (as hereinafter defined) and a caustic alkali in an amount sufficient to provide, when contacted with the free acids in the oil or fat, a

soapstock solution having a concentration suitable for fractionation, so as to give an intimate mixture, allowing sufficient time for a higher melting fraction to form a separable crystalline phase and then separating that phase from the lower melting fraction.

The present invention is concerned with the use of free fatty acids included in crude oils as a wetting agent. It is common in an oil refining process for the crude oils to be neutralized with an aqueous caustic alkali solution (this process is called "deacidification") and then separated into an oil layer and a water layer. The latter is then acidified to recover free fatty acids and the remaining mother liquor is then drained off. The crude fatty acids which are a by-product of the deacidification process are a complicated mixture of several fatty acids and a considerable amount of other impurities having very low commercial value. The fractionation is usually carried out on a pure or semi-pure oil from which all the free acids have already been removed by the deacidification process. Thus, to obtain a fractionated oil starting from crude oil (untreated raw oil) it has taken two separate processes, namely, deacidification and fractionation.

It has now been found that crude soapstocks derived from crude oil refining are unexpectedly useful for the fractionation of the oil. It is to be expected that soaps (alkali metal salts of higher fatty acids) have a good wetting action, but it is completely unexpected for crude soapstocks including various miscellaneous impurities to have an excellent wetting action. Utilization of crude soapstocks as the wetting agent means that:—

(i) a partial deacidification can be carried out simultaneously with the fractionation which facilitates succeeding refining processes,

(ii) water polluted with soap is comparatively harmless as evidenced over a period of several hundred years; consequently by using soap as the wetting agent it is possible to diminish current pollution problems,

(iii) in connection with the above item (ii), the amount of the waste water can be minimised, if the soapstock solution used is recirculated for the next fractionation,

(iv) caustic alkali, in particular, sodium hydroxide, which is the only material required for the process is one of the cheapest materials in industry. No other material is required since during operation of the process new free fatty acids are automatically supplied into the system in the new crude oil to be treated. Most crude oils include a sufficient amount of the free fatty acids for the process.

(v) as the aggregate effect derived from items (ii) and (iv) the manufacturing cost for the production of the fractionated oils can be reduced.

In performing the invention a caustic alkali in an amount sufficient to form the soap and an electrolyte are added suitably in the form of an aqueous solution to the oil, suitably a crude oil, in which at least part of the solid portion of said oils has been suspended or precipitated out, suitably by cooling. After a while the mixture of oils and the aqueous solution may then be separated into three portions, that is, a solid oil portion, a liquid oil portion and the remaining aqueous portion (the water layer) by known separating methods such as centrifugation. The aqueous portion is preferably then used again for the second fractionation process with a supply of new caustic alkali. Any further fractionation may be carried out in the same way as the second fractionation. Theoretically the polluted water layer from the first fractionation can be reused endlessly, but, in practice, such repeated use, e.g. use several times or more will usually make the viscosity of the layer too great because of the gradual accumulation of the soap-stock formed and gummy substances originating from the raw oils. Therefore, preferably, a small part of said layer is drained off from time to time, continuously or at regular intervals during the process.

The invention is illustrated by way of example in the accompanying Figure which represents a flow chart of a process in accordance with the invention.

In the Figure, a crude oil 1 is warmed to 50 to 60°C and pumped to a crystallization tank 2 provided with a cooler and a stirrer. The oil is then cooled slowly to a predetermined intermediate temperature with slow stirring until at least a small amount of crystals of the higher melting portion is precipitated out. Then, the cooled oily suspension is admixed with an aqueous solution consisting of a caustic alkali such as sodium hydroxide and an electrolyte such as sodium chloride in tank 2 and further cooled for a period of from 2—6 hours to a predetermined final temperature with slow stirring so as to accelerate the growth of large, uniform crystals of the higher melting portion. The viscosity of the mixture increases as the crystals develop. The suspension, containing an abundant amount of the crystals

being suspended, is then further mixed with the above aqueous solution in a mixing tank 3 provided with a stirrer. The amount of the aqueous solution to be added at this time is generally greater than that formerly added. The mixed suspension is then held for a while (usually 10 to 30 minutes) in this tank 3 with slow stirring. Thereafter, the mixture is pumped to a separator (a continuous centrifuge) 4, in which the mixture is centrifugally separated into two layers that is, an upper layer (U), composed of the liquid portion and a lower layer (L), composed of the crystalline solid portion, the electrolyte, the soapstock originally present and/or newly formed, water soluble impurities derived from the raw oil and water. Unlike experimental centrifuges, in industrial continuous centrifuges, phase separation between the middle and the lowest layers does not occur. Both the layers are removed together continuously from the machine. The layer U is then collected from the separator automatically by means of phase separation to recover the low melting glycerides 7. The layer L is removed from the separator and pumped to a heater 5 in which it is heated to 100 to 130°C, and finally pumped to a separator 6 wherein the mixture is re-centrifugated to be separated into the solid glycerides 8 and the remaining water layer (W). The latter is recirculated as shown by the dotted lines except that a small amount (W'') of it is continuously or incrementally drained off. (Optionally the water layer may be passed through the neutralization tank and centrifuge 9, 10, before recycling, as discussed hereafter). After the initial fractionation, the supply of the electrolyte into the system becomes almost unnecessary except for the introduction of a small amount of electrolyte corresponding to that amount of electrolyte which has been lost. However, the greater the number of times the water layer is recirculated the greater the viscosity of said layer because of gummy substances existing in the raw oils and further because the concentration of the soapstock in the system gradually increases step by step as much as the normal fractionation is disturbed. Therefore, in practice it is important that the concentration of the electrolyte and soapstock in the system is maintained within a definite range by means such as partial or entire replacement, or neutralization of the water layer (W). For example, the drained water (W) from the separator 6 may be neutralized with an acid in a neutralization tank 9 and isolated with a centrifuge 10 so as to recover the free fatty acids 11 and may then be reintroduced into the system as shown by the linked lines except that a small amount of the supernatant (W') is continuously or incrementally drained off. In this way, the amount of the electrolyte to be supplied can be saved depending on the amount which can be produced from the neutralization. Alternatively, tanks 2 and 3 may be consolidated into one, if desired. Alternatively, any soapstock which is the by-product of any deacidification process can be introduced into the system. For example, the soapstock solution obtained from refining laurin oils such as coconut oil is very useful for replacing the water layer to be circulated. These minor arrangements can be made by any expert in this field.

Any solid, semi-solid or liquid oil may be used as the raw materials of the present process, but, the most preferred material is a solid or semi-solid oil such as palm oil, lard, beef tallow, coconut oil, palm kernel oil or babassu oil. These oils are generally used in the crude form, but so long as they contain a significant amount of free fatty acids, semi-refined oils may also be used. The content of the free fatty acids can be measured by titration with alkaline solution which gives a definite individual acid value for each oil respectively. The preferred lower limit of the acid value is 0.5. An acid value below 0.5 will hardly give a good result without the addition of soapstock not formed *in situ* because the content of the free fatty acids is insufficient.

Any hydroxide of the alkali metals may be used as the caustic alkali in the present invention. However, the most preferred caustic alkali is sodium hydroxide because of its low price and because it provides sodium chloride when neutralized, which is the most common salt in nature.

The term "electrolyte" as used herein means a neutral, water-soluble salt of a strong acid and/or a strong base.

Any salts capable of strong dissociation can be used as the electrolyte in the present invention. Examples of electrolytes are sodium chloride, sodium sulphate, sodium nitrate, sodium phosphate, potassium chloride, potassium sulphate, potassium nitrate, potassium phosphate, ammonium chloride, ammonium sulphate, ammonium nitrate, ammonium phosphate, magnesium chloride and magnesium sulphate. Sodium chloride or sulphate are preferred.

The caustic alkali introduced into the system reacts with free fatty acids present in the raw oils to form alkaline soaps and the latter envelop the particles

(crystals) of the solid portion in the raw oil so as to decrease the interfacial tension between the solid and liquid portions, and consequently, facilitate the separation. In order to provide good separation the raw oils should be present in a crystalline suspension in which the higher melting portion is suspended in the liquid lower melting portion. In this connection, the crude oils are preliminarily warmed to form a homogeneous liquid, if said oils are solid, semi-solid or hardly flow at the ambient temperature. In general, the crude oil is warmed to a temperature of from 50 to 60°C. Then the homogeneous oil is slowly cooled until crystals of the higher melting glycerides (the solid portion) appear with slow agitation by which the development of large, definite crystals is accelerated. In practice the end temperature and cooling velocity are determined in accordance with the object of the fractionation. The lower the temperature is dropped the less is the amount of the lower melting portion.

Aqueous solutions of the caustic alkali and electrolyte or more preferably a single aqueous solution of alkali and electrolyte is then contacted with the above crystalline suspension. The amount of the caustic alkali should be sufficient to make up a soapstock solution which will cause the separation between the higher melting and lower melting portions of the oil. An appropriate concentration for said the caustic alkali solution is within a range of 0.03 to 0.5% by weight. If the concentration is far less than the lower limit, the soapstock solution formed is too dilute to effectuate the separation. On the other hand, if the concentration is far more than the upper limit, the separation is badly influenced because of the over-emulsification caused by such a high concentration.

The caustic alkali is usually added to the oil suspension in the form of an aqueous solution and conveniently, together with the electrolyte. Thus, the concentration of the caustic alkali present in the mixed aqueous solution can be determined readily on the basis of the mean molecular weight of the free fatty acids present in the crude oil, the proportion of the aqueous solution to the crude oil to be treated and the molecular weight of the caustic alkali. The following table shows some approximate data calculated with respect to a palm oil in which equal amounts of the crude oil and of the aqueous solution are admixed together.

Concentration of NaOH (%) by weight	Concentration of the soapstock formed (%) by weight	Estimated numbers of the acid value to be depressed
0.2	1.43	2.86
0.1	0.71	1.42
0.07	0.50	1.0
0.05	0.38	0.76
0.03	0.21	0.42

The electrolyte seems to act as a builder associating with the action of the soapstock. In addition to the caustic alkali, it is necessary to maintain the concentration of the electrolyte in the mixed aqueous solution during the separation. An appropriate concentration range is from 0.5 to 5.0% by weight. If the concentration is far less than the lower limit of said range, separation between the crystalline higher melting portion and the liquid lower melting portion is unsatisfactory. Also, too high concentration will also give unfavourable results because of the salting out action of the soapstock per se caused by the concentrated electrolyte.

The caustic alkali and the electrolyte, as hereinbefore explained, are usually applied to the crude oil as an aqueous solution. A mixed solution preferably contains 0.5 to 5.0% by weight of the electrolyte and 0.03 to 0.5% by weight of the caustic alkali. Preferably 0.5 to 2.0 parts by weight of this mixture is admixed with one part by weight of the crude oil wherein the solid portion thereof is suspended. But the amount of the mixture added should be controlled in accordance with the above recommendations. The addition of the aqueous mixture will lower the viscosity of the suspension. If the amount of the mixture added is too small the viscosity will not be lowered sufficiently to facilitate the separation. Alternatively,

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
Crude oil	8.64	—	51.7	38.1
Liquid portion	7.03	343	54.6	26.9
5 Solid portion	7.26	45	29.4	55.8
Loss	—	12	—	—

EXAMPLE 4.

The process of Example 1 was repeated using a different crude palm oil except that the crude oil was cooled to 20°C and 600 parts of an aqueous caustic alkali solution (containing 0.2% of sodium hydroxide and 4% of sodium chloride) were added to the crude oil to give the following data:

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
Crude oil	8.53	—	52.8	37.6
15 Liquid portion	6.05	273	58.6	17.2
Solid portion	6.52	116	38.6	50.4
Loss	—	11	—	—

EXAMPLE 5.

400 parts of a crude palm oil were warmed to 50°C and were subsequently cooled with slow stirring. When the temperature of the oil reached 35°C a small amount of crystals precipitated out.

40 parts of a caustic alkali solution (containing 0.07% of sodium hydroxide and 2% of sodium chloride) were poured into the crude oil at this time and the oil was further cooled to 22°C. The oil was held at this temperature for two hours to fully precipitate out the crystals. Thereafter 360 parts of the above caustic alkali solution were added to the oil which was left for another 10 minutes. The resulting dispersion was treated as in the above examples to give the following data:

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
30 Crude oil	8.32	—	51.4	38.4
Liquid portion	7.40	290	57.4	19.2
Solid portion	7.51	99	33.9	52.4
Loss	—	11	—	—

WHAT WE CLAIM IS:—

1. A method of fractionating oils and fats which method comprises contacting a suspension of a solid higher melting fraction of an oil or fat in a liquid lower-melting fraction, the oil or fat containing free fatty acids, with an aqueous solution comprising an electrolyte (as hereinbefore defined) and a caustic alkali in an amount sufficient to provide, when contacted with the free acids in the oil or fat, a soapstock solution having a concentration suitable for fractionation, so as to give an intimate mixture, allowing sufficient time for a higher melting fraction to form a separable crystalline phase and then separating that phase from the lower melting fraction.

2. A method of fractionating oils and fats as claimed in claim 1, wherein the aqueous solution is separated from the oil or fat after fractionation and at least

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
Crude oil	8.64	—	51.7	38.1
Liquid portion	7.03	343	54.6	26.9
5 Solid portion	7.26	45	29.4	55.8
Loss	—	12	—	—

EXAMPLE 4.

The process of Example 1 was repeated using a different crude palm oil except that the crude oil was cooled to 20°C and 600 parts of an aqueous caustic alkali solution (containing 0.2% of sodium hydroxide and 4% of sodium chloride) were added to the crude oil to give the following data:

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
Crude oil	8.53	—	52.8	37.6
15 Liquid portion	6.05	273	58.6	17.2
Solid portion	6.52	116	38.6	50.4
Loss	—	11	—	—

EXAMPLE 5.

400 parts of a crude palm oil were warmed to 50°C and were subsequently cooled with slow stirring. When the temperature of the oil reached 35°C a small amount of crystals precipitated out.

40 parts of a caustic alkali solution (containing 0.07% of sodium hydroxide and 2% of sodium chloride) were poured into the crude oil at this time and the oil was further cooled to 22°C. The oil was held at this temperature for two hours to fully precipitate out the crystals. Thereafter 360 parts of the above caustic alkali solution were added to the oil which was left for another 10 minutes. The resulting dispersion was treated as in the above examples to give the following data:

	Acid Value	Yield (parts)	Iodine Value	Melting Point (°C)
30 Crude oil	8.32	—	51.4	38.4
Liquid portion	7.40	290	57.4	19.2
Solid portion	7.51	99	33.9	52.4
Loss	—	11	—	—

WHAT WE CLAIM IS:—

1. A method of fractionating oils and fats which method comprises contacting a suspension of a solid higher melting fraction of an oil or fat in a liquid lower-melting fraction, the oil or fat containing free fatty acids, with an aqueous solution comprising an electrolyte (as hereinbefore defined) and a caustic alkali in an amount sufficient to provide, when contacted with the free acids in the oil or fat, a soapstock solution having a concentration suitable for fractionation, so as to give an intimate mixture, allowing sufficient time for a higher melting fraction to form a separable crystalline phase and then separating that phase from the lower melting fraction.

2. A method of fractionating oils and fats as claimed in claim 1, wherein the aqueous solution is separated from the oil or fat after fractionation and at least





1,490,551

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if the amount is too large, the amount of the oil-water suspension becomes too large to be treated. The proportions of the aqueous mixture to the crude oil given above represent a practical range in this respect.

The waste water removed from the system contains mainly the electrolyte used or formed, the soapstock or the free fatty acids, and a minor amount of organic ingredients. The soapstock may be acidified to recover the corresponding free fatty acids. The remaining water may be passed safely into the sea or sewer-pipe through a conventional clarifier such as a bubble-foaming apparatus with or without coagulant or precipitant.

The present invention is further illustrated by way of example with reference to the following examples in which percentages are given by weight.

EXAMPLE 1.

400 parts of crude palm oil warmed to 50°C was slowly cooled to 22°C over a period of 4 hours with slow stirring. The oil was then allowed to stand for two hours at the same temperature to completely precipitate out the crystalline portion.

400 parts of caustic alkali solution (containing 0.07% of sodium hydroxide and 2% of sodium chloride) were poured into the cooled oil and the mixture was slowly stirred for 15 minutes and then centrifugated to form three layers, namely, an oily upper layer, an intermediate crystalline layer and a lower water layer. The upper layer composed of the liquid oil portion was removed from the centrifuge and the remaining two layers were heated together to 100°C, and separated centrifugally into an oily layer (the solid oil portion) and the water layer. Details of this fractionation are as follows:

	Acid Value	Yields	Iodine Value	Melting Point
		(parts)		(°C)
Crude oil	8.70	—	51.4	38.4
Liquid portion	7.80	288	57.2	19.2
Solid portion	7.92	99	34.2	51.3
Loss	—	13	—	—

EXAMPLE 2.

Another crude palm oil was processed as described in the prior example to give the following data:

	Acid Value	Yields	Iodine Value	Melting Point
		(parts)		(°C)
Crude oil	7.38	—	52.6	37.6
Liquid portion	6.42	307	57.6	18.7
Solid portion	6.48	83	35.1	51.4
Loss	—	10	—	—

EXAMPLE 3.

The process of Example 1 was repeated using a different crude palm oil except that the crude oil was cooled to 32°C over a period of 3 hours and 300 parts of aqueous caustic alkali solution (containing 0.2% of sodium hydroxide and 4% sodium chloride) were added to the crude oil to give the following data:



1,490,551

- part of the aqueous solution is recirculated to provide a component of the aqueous solution comprising a caustic alkali and an electrolyte which is added to the oil or fat to be fractionated.
3. A method of fractionating oils and fats as claimed in claim 1 or claim 2 wherein soapstock solution produced by any oil or fat refining process is introduced to the aqueous solution of a caustic alkali and an electrolyte which is added to the oil or fat to be fractionated and used as one component thereof.
4. A method of fractionating oils and fats as claimed in claim 2 or claim 3, wherein at least a part of aqueous solution is recirculated after every fractionation cycle to provide a component of the aqueous solution which is added to the oil or fat to be fractionated.
5. A method for fractionating oils and fats as claimed in any one of the preceding claims, wherein the caustic alkali is sodium hydroxide.
6. A method for fractionating oils and fats as claimed in any one of the preceding claims wherein the electrolyte is sodium chloride or sodium sulphate.
7. A method for fractionating oils and fats as claimed in any one of the preceding claims wherein the aqueous solution contains 0.03 to 0.5% by weight of a caustic alkali and 0.5 to 5.0% by weight of an electrolyte.
8. A method for fractionating oils and fats as claimed in any one of the preceding claims wherein the aqueous solution of a caustic alkali and an electrolyte is added to the suspended oil or fat to be separated in a weight ratio of 0.5 to 2.0:1.0.
9. A method for fractionating oils and fats as claimed in any one of the preceding claims wherein the concentration of the soapstock solution formed by the addition of the caustic alkali to the oil or fat is 0.2 to 3.5% by weight.
10. A method of fractionating oils and fats substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.
11. A method of fractionating oils and fats substantially as hereinbefore described in any one of the specific Examples.
12. Fractionated oil or fat whenever prepared by a method as claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.