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PROCESS FOR THE PURIFICATION OF HARD FATS

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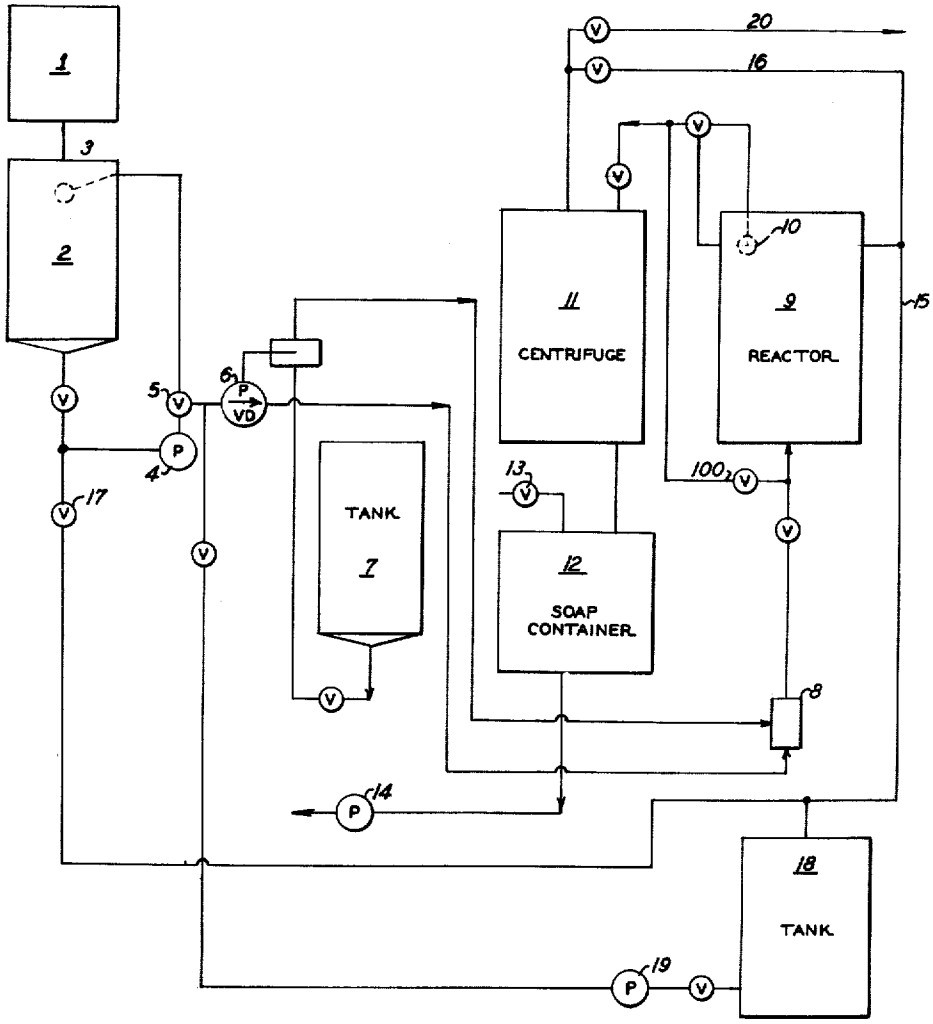


Fig. 1

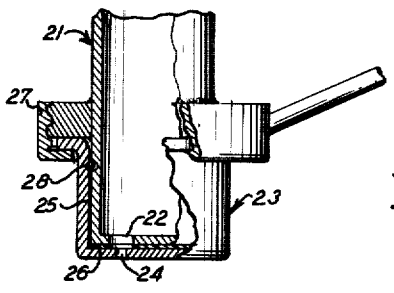


Fig. 2

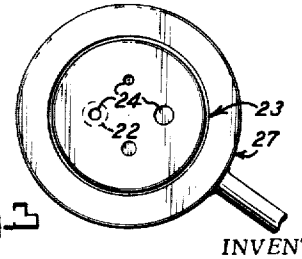


Fig. 3

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PROCESS FOR THE PURIFICATION OF HARD FATS

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This invention relates to improvements in the refining of solid fats. The invention, more particularly, relates to the deacidification of oils and fats of animal and vegetable origin, which fats are solids, at temperatures of 18–20° C. The invention is a continuation-in-part of application Serial No. 526,146, filed August 3, 1955, and now abandoned.

In order to render animal and vegetable fats useful for human consumption, various successive refining process steps must be effected, as for example slime removal, deacidification, bleaching and deodorization. Of these refining steps the deacidification process has as its object the removal of the free fatty acids substantially down to a residual content of less than 0.1% and the elimination as far as possible of the accompanying substances, which impart an undesirable taste, odor and color to the oil. Among these accompanying substances there may be included, for example, metallic colloidal nickel, which often remains in the crude solid fat after the hydrogenation process, and, as is well known, may have an extremely injurious effect on the fat.

The most customary method for effecting the deacidification is with alkali. In accordance with the originally used process, the deacidification was effected intermittently in large settling tanks and the soaps which formed, which were also known as soap stock, were dissolved to a greater or lesser extent with hot water, whereupon the soap solutions were manually withdrawn after having been set aside.

In accordance with later developments, the so-called soap-stock centrifuges have often been used to continuously separate and discharge the soaps precipitated with the alkalis.

Both of these methods, however, have the disadvantage that traces of moist soap still remain in the oil. These traces must be removed, so as not to interfere, for example, with the subsequent bleaching process, using fuller's earth or bleaching carbon. The activity of the bleaching agent will otherwise be reduced, and filtering difficulties will occur.

The impermissible amount of soap stock, which often remains in the oil even after the centrifugal soap stock separation, is due to various factors. If concentrated caustic solutions are used for the deacidification, soap flakes which contain water are produced. If this mixture of oil and soap flakes is subjected to centrifugal force, the soap flakes do not completely combine to form a flowable mass, but the flakes of lighter specific gravity are carried along with the oil. At the same time, depending upon the type of oil, larger or smaller quantities of soap are dissolved in the oil and therefore cannot be separated. This is particularly true if the oil has a high water-binding power. Additionally, traces of accompanying materials, as for example lecithins, increase the solubility of the soap in the oil or hold the soap firmly bound as fine suspensions in the oil. It should also be noted that the separated soaps contain a certain quantity of the neutral oil, resulting in the loss of this valuable product.

If the soap is diluted with water or if dilute alkali is used, for example, in order to obtain soaps which contain less neutral oil or to improve the flowing properties of the soap, emulsions of oil and soap solutions are readily produced, which upon separation are also discharged in the form of fine dropline along with the oil. The water-containing soap traces must, in accordance with the prior known methods, be washed out of the oil with hot water. The wash-water is either allowed to stand and manually drawn off or is separated by means of a so-called wash centrifuge. A single washing in many cases will not suffice and multiple-stage washings become necessary, particularly in connection with those oils having a high water-binding power and which retain the soap residues so stubbornly that quantities of water of 10% or more, referred to the quantity of oil, are often required. This method requires a considerable expenditure of time and a relatively elaborate apparatus set-up. Further, the heat of the water used for the washing is lost along with quantities of neutral oil, which both at times are considerable.

It has also been proposed to deacidify oils with alkali under vacuum and to dry the soaps produced in this connection. The soaps so produced, however, are finely granular, and the separation of this granular product from the oil involves considerable difficulties. Water-free or water-poor soaps so produced are not capable of flowing and their specific gravity is frequently only slightly higher than that of the oil. As a result of this, both the separation of the soaps from the oil and the removal of the soaps from the centrifuge is made considerably more difficult. The dry soap flakes obtained, therefore, have to be made viscous and flowable by suitable additions, such as by water or salt solutions, so that the same may be removed from the centrifuge. As an alternative, the specific gravity of the soap has to be increased by the addition of fuller's earth or bleaching carbon in order to be able to separate the soap by centrifugation. Aside from the fact that the production of the dry soap flakes by vacuum is cumbersome from an apparatus standpoint, as for example foaming must be prevented by the installation of agitators, etc., this method was not satisfactory, since on the one hand it was still necessary to again wash the oil, due to an unsatisfactory separation of the soap, and on the other hand the addition of the substances required to effect the centrifuging of the soap flakes proved disturbing and caused additional expenses.

For these and other reasons the vacuum treatment has not found general acceptance, and the first mentioned processes, despite their known disadvantages in view of the washing stages, are still the most widely used. Thus, prior to the instant invention, it has not been possible to obtain in a single treatment stage in the deacidification of oils and fats a product which is ready for bleaching.

It is an object of the present invention to provide a novel process for refining solid animal and vegtable fats to remove fatty or non-fatty impurities, or both.

Another object of the present invention is a new process for the purification of solid animal and vegetable fats, which allows in a single treatment stage a product ready for bleaching.

Still another object of this invention is to provide a refining process for animal and vegetable fats, which minimizes refining losses, making possible a recovery of as much of the purified fats as possible.

These and other objects will be apparent to those skilled in the art from the following description of the invention and of the best presently known manners of practicing it.

In the drawings

FIG. 1 diagrammatically illustrates one of the plant

set-ups, by which the invention can be performed and is in the form of a flow sheet;

FIG. 2 is a view, half in section, of the form of apparatus for regulating the diameter of the alkaline reagent liquid stream; and

FIG. 3 is a bottom view of the structure illustrated in FIG. 2.

In accordance with the present invention it has been discovered that the disadvantages of the known processes for purification of oils and fats by deacidification with a sodium hydroxide solution can be substantially avoided by careful regulation of the manner of the addition of the sodium hydroxide solution to the molten fat and oil. By the process of the invention the sodium hydroxide solution is added to the molten fat in such a manner that the particles of the sodium hydroxide solution, when the same is added in a dropwise manner, at the moment of contact with the fat are not smaller than 0.2 mm. in diameter and do not exceed 5 mm. in diameter and when the alkali hydroxide solution is added in the form of continuously flowing stream, then the diameter of the stream falls within the range of 0.2 mm. to 5 mm. The quantity and concentration of the sodium hydroxide solution used contains at least that amount of sodium required to effect the neutralization of the fatty acids present in the fat, and further, the amount of water introduced with the sodium hydroxide solution is at most that great that the water content of the soap formed by action of the sodium does not exceed the 1.5-fold weight of the soap. This water includes the water introduced with the reactants (alkali hydroxide solution and fat, if the latter should contain any water) and the water formed during the soap formation. The mixture of sodium hydroxide solution and molten fat is then stirred, but only to that extent required to effect an intimate contact of all of the molten fat and sodium hydroxide solution, care being taken that no emulsification occurs or shattering of the soap particles formed. As a result of the mixing, a soap stock is produced, which is coarsely granular and has a single-phase structure. The term "single-phase structure," as used herein and in the claims, is intended to designate that the water in addition to any possible impurities etc. are firmly bound to the soap and do not occur as a second soap phase separate from the soap. The soap stock thus formed is then centrifugally separated from the molten oil and/or fat without the use of any scrubbing or washing stages. In accordance with the invention, the deacidification of the fats and oils is effected with an alkali hydroxide solution of high concentration containing between about 8 and 40% by weight of alkali hydroxide, and preferably sodium hydroxide. It is also preferable if the oils and/or fats are simultaneously mixed with a material having an affinity for chemically binding water, as for example dry sodium chloride.

Suitable fat materials for the practice of the invention include fatty acid esters, which are solids at temperatures of from 18–20° C. and whose fatty acid components in free, i.e., unesterified, form have melting points of at least 27° C. and preferably of from 30–45° C. The fatty acid esters are of both natural and synthetic origin, but preferably of natural origin. The fatty acid esters, which may be used in accordance with the invention, may exist in their original state as solids. However, fats which are "hardened," as for example by hydrogenation procedures, are also suitable. Thus, it is possible to convert fat materials which do not normally exist in the solid state into solid materials and to process the same further in accordance with the invention. Hardened fats, in which for example metallic colloidal nickel still remains from the hydrogenation process, benefit especially from the process in accordance with the invention.

Natural fatty acid esters are obtained from the fat of vegetable and land and marine animals. Examples of the various types of vegetable fats include coconut oil, palm oil, olive oil, soy bean oil, linseed oil, wood oil and rapeseed oil. Examples of the various types of fats obtained from land animals include beef fat, hog fat and bone fat. Examples of the various different types of fats of marine animals include whale oil, menhaden oil, cod liver oil and herring oil. Preferably, the fatty acid esters to be processed are glycerides. However, fatty acid esters which contain alcohols other than glycerine as the alcohol component may serve as the starting material in accordance with the invention.

The exact minimum concentration of the alkali hydroxide solutions, which may be used in accordance with the invention, depends somewhat on the average molecular weight of the free fatty acids contained in the fats and the oils being treated. If, for example, the free fatty acids have an average molecular weight of about 280, the minimum concentration of the caustic solution employed should be about 8% by weight alkali hydroxides, such as sodium hydroxide. If fats, having a free acid content with an average molecular weight of about 200, as for example coconut fats, are being refined, the minimum concentration of the caustic solution should be about 11% by weight NaOH. Since these fats at times contain larger or smaller quantities of water, and since water is produced in the deacidification itself, it is advisable to operate with high concentrated caustic solutions of, for example, 14 to 40% by weight NaOH and advantageously about 25 to 30% by weight NaOH. If these caustic solutions also contain salt, the concentration of the dissolved sodium chloride may be increased up to the saturation concentration, but good results are obtained even at lower concentrations. A caustic soda solution of, for example, 18% by weight NaOH can, for example, contain 4% by weight NaCl.

Caustic solutions of higher concentration of for example up to 40% by weight NaOH may be used not only in the case of water-containing oils and fats, but also in the case of oils and fats having a particularly high water-binding power, as for example in the case of various types of crude solid fats.

Temperatures of the oils and fats to be deacidified can vary between about 30 and 100° C. during the addition of the alkali hydroxide solutions. The optimum temperature for any given oil or fat under any particular refining conditions may be easily determined.

It is essential that, when adding the alkali hydroxide solution to the oil, care be taken to ensure that the particles of the alkali hydroxide solution or liquid stream at the time of contact are not smaller in their smallest dimension than 0.2 mm. Preferably the smallest dimension of the particles of the alkali solution, as for instance the diameter of the particle or stream, is not larger than 5 mm. In allowing the alkali solution to drip onto the oil surface, the height of fall should not be too great in order to avoid spattering of the solution, whereby the same becomes distributed in the oil in the form of droplets which are too small. Preferably, the diameter of the flow of the alkali hydroxide solution is regulated so that the solution just exceeds the status of the drop and impinges in the form of a thin coherent stream on the surface of the oil. The diameter of the stream is directly dependent on the amount of solution added and must lie within the range of 0.2 to 5 mm. This requirement may technically be easily accomplished by providing the supply line for the alkaline solution at its end with a revolving rim of capillaries of various diameters, of which in each case the one corresponding to the alkali solution throughput is in operating position. Furthermore, it is expedient to leave the outflow end of the supply line a small distance above the surface of the oil, care being taken that with fluctuations in level, brought about in the operation, no contact takes place between the outflow opening and oil. Thus, there is avoided any deposition of sediments at the pipe-end and/or cloggings through soap formation.

The quantity of sodium hydroxide solution added must

be at least equivalent to the quantity of the existing free fatty acid. Preferably, there is employed at least a small excess of sodium solution, and it is preferable to employ one of about 10%. However, sodium solutions in great excess may be employed, in order to obtain in addition to the deacidification a removal of impurities from the ester. The excess may amount to up to 500%, referred to the stoichiometric amount of sodium solution necessary for the conversion of the free fatty acid to soap. The time of stay being necessary for the formation of single-phase coarse soap particles is at least 5 minutes. In most cases, it is advisable to extend the time of action to 15–30 minutes in order to obtain an advantageous purification of the oil by the separation of accompanying substances.

Insofar as the amount of sodium hydroxide solution does not essentially exceed the amount stoichiometrically necessary for the conversion of the free fatty acid into soap, that is, the amount of sodium hydroxide solution amounts to at most 110% of this quantity, a comparatively short time of stay in the reaction vessel of 5 minutes is sufficient to completely react the free fatty acid and sodium hydroxide solution with each other. However, if larger quantities of sodium hydroxide solution are used, the sodium solution and the oil must remain in contact with each other for a sufficiently long time so that the excess of alkali can be removed by saponification with neutral oil. The saponification of the excess alkali must take place to such a degree that the alkali solution still present no longer exerts a salting-out effect on the soap, so that the coarse-grained mono-phase soap formation is not interfered with. For the saponification of neutral oil by the excess alkali, the time of stay must of course be extended and is dependent in each case on the amount of the excess and the treatment temperature. The reaction time may amount to 15–30 minutes, and may also be extended to times of 1 to 2 hours.

For the purposes of the deacidification there may be employed as the alkali agent, sodium hydroxide. Additionally water glass solutions have been satisfactorily used.

The reaction temperature selected must in each instance lie above the melting point of the oils and fats to be deacidified and can vary between about 30–100° C. Optimum results have been obtained with temperatures of between 60 and 75° C.

It is also possible to vary the temperature during the reaction. Thus, for example, the alkalis can be added to the oil at 100° C., followed by cooling to 30° C., or vice versa. Similarly, the pressure may be varied during the reaction. It is preferable to effect purification under atmospheric pressure or slight excess pressures, such as are automatically produced in the reactor. On the other hand, it is advisable to avoid operation under reduced pressure, as the same causes a too finely granular structure of the soap stock, reduces the specific gravity of the same and tends to cause foaming.

The alkali solutions may be added intermittently or continuously, and should be intimately mixed with the oils and fats, care being taken that no emulsification occurs. The water-binding material, such as the common table salt, may be added simultaneously with the alkali in the form of a solution. It is, however, also possible to add the same in solid form. In both cases, there are obtained coarsely granular single-phase soap structures if, as a result of a suitable concentration of the caustic solution, the indicated water content of the soap is not exceeded.

In connection with the water-binding material, in place of the sodium chloride, there may also be utilized calcium chloride, sodium carbonate, etc.

The mixing of the alkali and oil is preferably effected in a reaction vessel, which assures the necessary time of stay and which is provided with an agitator which will assure uniform mixing throughout the entire vessel without causing emulsification. It has been found preferable to use the reaction vessel, as described in copending application Serial No. 526,145, filed August 3, 1955, in which the agitator consists of a worm extending throughout the length of the reaction vessel and is divided into adjacent segments of reversed pitch. In this manner a uniform mixture of the alkali and oil is obtained without any emulsions being formed.

Due to the fact that the soap stock produced in accordance with the invention is of a coarsely granular single-phase structure, and has an extremely favorable specific gravity and has adsorbed the customary substances to a high extent, it may easily be retained in the sludge space of a centrifuge, and the oil emerging from the centrifuge will be clean and will contain at the most a few hundredths of a percent of soap and moisture. It can then be further worked without washing or drying, as for example bleached with fuller's earth. The soap produced and separated in this manner is highly concentrated and contains only a very small amount of neutral oil. In order to prevent oxidation of the oil being treated or from other possible damage to the fat caused by exposure to the air, the entire treatment is preferably carried out under exclusion of air.

The process in accordance with the invention is preferably effected in a plant set-up corresponding to the one diagrammatically shown in the accompanying drawing.

The crude oil, which is to be refined, passes from a storage container or a filter press **1** into a temperature-control vessel **2**, in which it can be heated or cooled. The temperature-control vessel **2** is provided with a level regulator **3**. The oil, which has been imparted the correct temperature, passes via a centrifugal pump **4** and a level-control valve **5** into the proportioning machine **6**. The level regulator **3** and the level-control valve **5** assure that the same level is obtained, even when the flow into the temperature-control vessel **2** differs. From container **7**, the alkali solution also passes through the proportioning machine **6** and is admixed with the oil by the injector nozzle **8**. The mixture enters the reactor **9** from the bottom, rises toward the top and leaves it via the float valve **10**. From there it passes by gravity to the separating centrifuge **11**. The soap-free, dry oil is discharged via conduit **20**. It can pass to a storage tank or be fed for continuous further processing to the next treatment stage. The soap is periodically removed from the centrifuge and drops into the soap container **12**, into which water for purposes of dilution can be introduced through the valve **13**. The soap pump **14** conveys the soap solution to a collecting tank. The lines **15**, **16** and **17** are by-pass and overflow lines, respectively, which in case of excess conveyance or disturbance of the equipment conduct the treatment material or the oil into the tank **18**, from which it can be returned to the operation by means of a centrifugal pump **19**.

In order to ensure that the alkali solution is fed to the oil in a liquid stream of specific diameter, a device as shown in FIGS. 2 and 3 is attached to the alkali solution supply line. The alkali solution supply line **1** is closed at its lower end by a flat disc or plate having an excentric bore hole therein. Inserted over the lower end of supply line **1** is a cap **4**, which is provided at its bottom-most part with several bore holes positioned in a circumferential arrangement and which cap is capable of being rotated about supply line **1**. On rotation of the cap, each of the openings is brought in turn into congruence with the excentric bore hole at the lower and closure end of the supply line **1**. The outer surface of the flat disc closure of the supply line and the corresponding inner surface of the cap are suitably machined so as to provide the necessary coincidence. There may be inserted a packing **5**, which may for example be made of Teflon (tetrafluoropolyethylene), between the cap and the end of the supply line. When it is necessary to change the diameter of the liquid stream, then the cap is loosened and the clamping screw **2**, made as a set screw, is used to turn the hole-containing cap into the desired position, in which it is held by means of retaining spring **3**, and then it is again clamped tight.

The openings in the cap 4 may be extended in the form of capillary tubes of corresponding diameter.

By the process in accordance with the invention it is possible to continuously or intermittently deacidify in a single-stage all fatty acid esters, and in particular all oils and fats with the exception of those which, for reasons of quality, require a further alkali treatment, in such a manner that the content of free fatty acid is reduced to less than 0.1%. In this connection, the soaps produced are removed together with the customary accompanying substances by means of a centrifuge from the oils to such a far-reaching extent that the oils deacidified in this manner do not need to be washed or dried for the following refining process, as for example bleaching with fuller's earth or bleaching carbon.

The water content of the soap stock formed in accordance with the invention is firmly bound to the stock in amount up to 1½ times the weight of the soap. This quantity of water, in conjunction with the water-binding materials, is sufficient to combine the soap produced into firm conglomerates. Since the entire water content is bound to the soap, the solubility of the soap in oil is also reduced to an insignificant value. Furthermore, the specific gravity of the soap structure is increased, which aids in the centrifugal separation. It is these properties that make possible a practically complete separation of the soap from the oil in accordance with the invention. For the centrifugal separation it is preferable to use desludging or clarifying centrifuges, from which the firmly pressed soaps may be periodically discharged.

The melting or softening points, as selected in the following examples, were determined according to the AOCS official method Cc 3–25 (softening point). The tests for nickel were carried out according to the standard methods of the German Society for Fat Research, C–II 9 (53). The soap contents were calculated on the basis of the titrimetrically ascertained content of soap alkali after drawing off free alkali possibly present and under the assumption that the fatty acid bound in the soap was stearic acid. If any other acid was used, as the basis for the calculation of the soap content, the same is set forth in the example. In some cases, the content of free alkali in addition to the content of soap alkali has been ascertained, possibly while there was also still present very small amounts of free fatty acids in the oil. Free fatty acids and free alkali are, of course, only stable in the presence of one another in a two-phase system, that is, when there is still included free alkali in the soap granulates. The determination of the free alkali and additionally the free fatty acid is accomplished in such systems in the following manner:

The alkaline soap is filtered off from the hard fat and the filtrate is then analyzed titrimetrically for free fatty acids. Another unfiltered sample of the fat is then dissolved in a suitable solvent, as for example a mixture of benzol and methanol, whereby the two-phase system is destroyed. This process may be accelerated through vigorous stirring or rotating of the titrating plungers. Then the content of soap and free alkali is determined by titration. Since in this second titration free alkali and free fatty acids react together, the values found must be corrected by means of those values ascertained in the first titration procedure.

The following examples are given by way of illustration and not limitation.

Examples 1–12

In each instance, 5000 kg. of the fats listed in the following table were hardened with hydrogen, employing nickel as catalyst, and were processed in the following manner after the catalyst had been filtered off.

The molten fats were introduced from the bottom into a reaction vessel, as is described in patent application Serial No. 526,145, with the aid of a dosing device. As alkaline reagent was then added a caustic soda solution consisting of 29 weight-percent NaOH in the form of a fluid stream of 1 mm. in diameter. The mixture of alkali solution and oil was then processed by slow movement of the stirring device. After a time of stay of 20 minutes the oil-soap mixture was passed continuously to a centrifuge. The sludge was removed at periodic intervals, without thereby interrupting the operational process. In the course of the process there were samples drawn from time to time from the purified product, which were analyzed. In the following table are given the average values. Deviations from these average values amounted at most to hundredths of a percent. The table additionally contains all the data important in the carrying out of the process. In the case of the hardened coconut and palm-kernel fats, in calculating the content of free fatty acids and of soap, there was taken as a basis the molecular weight of lauric acid (200). In all of the purified fats, absolutely no nickel could be detected, while in all instances the starting materials contained small amounts of nickel. The purified products were clear and had a moisture content of below 0.1% so that they could be further bleached with bleaching earths without any additional washing and drying steps. The soaps, periodically extracted from the centrifuge, were highly concentrated, solid and crumbly. They were treated in a collecting vessel with hot water and decomposed in the conventional manner with sulfuric acid. The purified fatty acids obtained in this manner had in no instance a melting point, which was lower than 27° C. The consumption of caustic solution was less than in the previously customary deacidification processes.

1	2	3	4	5	6	7	8
Example No.	Natural fat, obtained from the starting material through hardening	Melt. point, ° C.	Content of free fatty acids, percent	Temperature of the purification, ° C.	Used NaOH of the stoichiometrically required amount, percent	Soap in the purified oil, percent	Free fatty acids in the purified oil, percent
1	Whale oil	32	0.29	68	193	0.009	0.035
1a	do	32	0.76	63	146	0.024	0.036
2	do	40	0.32	70	200	0.012	0.032
2a	do	40	1.01	63	134	0.030	0.039
3	do	46	0.59	73	183	0.030	0.045
4	Fish oil	34	0.25	68	272	0.009	0.028
4a	do	34	0.62	66	140	0.012	0.046
5	do	40	0.48	64	156	0.012	0.034
6	Sperm whale oil	37	0.28	63	214	0.015	0.030
7	Cottonseed oil	32	0.20	62	315	0.012	0.032
8	do	37	0.31	66	242	0.015	0.028
9	Peanut oil	30	0.17	73	300	0.009	0.021
10	Sunflower oil	32	0.25	66	200	0.012	0.039
11	Palm kernel oil	32	0.14	70	321	0.015	0.028
12	Coconut oil	27	0.11	62	464	0.018	0.056

NOTE.—The values reported in columns 7 and 8 and elsewhere in the specification are accurated to the third decimal place.

Example 13

In the manner described in the previous examples, 6000 kg. of fish oil, hardened to a softening point of 33° C., with a content of 0.3% of free fatty acids, were treated at 67° C. The crude fat was deacidified by adding the alkali hydroxide solution to the oil in two portions. This made for two purification periods, of which each purification period lasted 15 minutes.

In carrying out the process, the amount of alkaline solution was from time to time in the second step increased so that it was no longer fully used up for the saponification of neutral oil. As may be seen from the following table, there were formed thereby alkaline soaps. It can also be seen from the table that preferably the quantity of the alkali addition and/or the time of contact between alkali and oil is so standardized that the free alkali content of the soap flakes is not higher than 20%, referred to the total alkali. However, any quantity of the free alkali possibly still contained in the purified fat after the separation is not stable and disappears on prolonged storage either through reaction with traces of free fatty acids possibly still present or through saponification of neutral oil. The results obtained have been listed in the table.

1		2	3	4
Alkali solution added, referred to the starting oil, calculated as soap		Free NaOH referred to total alkalinity, percent	Soap in the purified fat after the separation of the soap, percent	Free fatty acid in the purified fat, percent
In the first step, percent	In the second step, percent			
0.54	0.07	0	0.018	0.050
0.54	0.29	12	0.018	0.039
0.54	0.39	20	0.027	0.014
0.54	0.84	25	0.056	0.000

Example 14

This example demonstrates the effect of the addition of common salt to the alkali solution. As starting material there was treated a whale oil hardened to a softening point of 32° C., containing 0.28% free fatty acids. Various portions of this oil were in each case stirred up with the same quantity of a caustic soda solution consisting of 14.5% NaOH, which amounted to 200 weight-percent times the stoichiometric quantity required for the neutralization of the free fatty acids. The individual portions of alkaline solutions contained varying quantities of NaCl dissolved therein. The solution was allowed to drip, drop by drop, at a drop diameter of 4–5 mm. and a height of fall to the surface of the oil of 5 cm. and was subsequently stirred for 20 minutes at 70° C. with a stirring apparatus, which made two to three revolutions per second. The speed of rotation sufficed to obtain a good distribution of alkali solution and oil without, however, shattering the particle of the alkali solution or the formed soap particles. After 20 minutes of stirring, the soap formed was separated from the oil centrifugally. The oil was then analyzed for soap and free fatty acid content. The values found are listed in the following table:

1	2	3
NaCl in the aqueous caustic solution, percent	Free fatty acid in the purified product, percent	Soap in the purified product, percent
4	0.021	0.020
8	0.016	0.010
12	0.025	0.000
16	0.020	0.000

Example 15

A palm oil, deacidified by distillation, was allowed to become partially solidified by cooling to room temperature. The solid constituents were separated and were found to have a melting point of 42° C. The constituents of the palm oil, which had remained liquid, were hardened with hydrogen, employing nickel as catalyst, until the product had a melting point of 38° C. This hardened fat was employed as starting material.

6000 kg. of this material, which still contained 0.2% free fatty acids (calculated as palmitic acid) were purified in the manner described in Examples 1–12 with caustic soda solution having a concentration of 29 weight-percent NaOH. The quantity of the solution added amounted to 250% of that theoretically necessary for the neutralization of the free fatty acid. During the treatment, the caustic soda solution added was substantially completely used up, so that the soap formed could be considered as alkali-free. After centrifuging off the formed mono-phase coarse-gained soap, a clear oil was obtained. Samples thereof, taken from time to time, had soap contents within the range of 0.012–0.018%. The oil thereof could be bleached without any further washing or drying processes.

The soap, periodically discharged from the centrifuge, was solid and dry. The soap was dissolved in hot water, and then decomposed with sulfuric acid. The fatty acid contained therein, determined after the mineral acid had been washed out and the fat had been dried, had an acid number of 150, a saponification number of 201 and a melting point of 39.5° C.

Example 16

As starting material there was employed the solid fat, as separated from the palm oil described in Example 15, having a melting point of 42° C. and a content of free fatty acids of 0.18% (calculated as palmitic acid).

200 weight parts of this fat were mixed for 20 minutes at 70° C. with 195% of the theoretically required quantity of caustic soda solution having a concentration of 23.5 weight-percent NaOH under substantially the same conditions as described in Example 14. The separation of oil from soap was effected in a bucket centrifuge. The oil obtained had a content of 0.010% soap and 0.050% free fatty acids. The soap was mono-phase and coarse-grained and had a specific weight greater than that of the molten hard fat, so that it could be easily directly separated from the latter.

Example 17

From crude coconut oil there were separated those components solid at room temperature. These had a melting point of 30° C. This fat was hardened until it had an iodine number below 1.

5000 kg. of this hardened coconut oil fraction with a content of 0.25 weight-percent free fatty acids (calculated as lauric acid) were purified at 61° C., with a caustic soda solution of 29 weight-percent NaOH in the manner described in Examples 1–12. The quantity of caustic solution added amounted to 280% of that stoichiometrically required on the basis of the content of free fatty acid.

The oil purified in this manner was completely clear and dry. Nickel residues could not be ascertained. The content of soap amounted to 0.015%, and the content of free fatty acids to 0.031%.

Example 18

Crude beef tallow having a content of free fatty acids of 0.2% was processed at 60° C. with a caustic soda solution consisting of 14.35% NaOH under the same conditions as described in Example 14. The quantity of the soda solution amounted to 250 weight-percent of the stoichiometrically required quantity. The treatment of the oil and the separation of the soap formed was under-

taken at 60° C. Also in this case, a coarse-grained, monophase soap was formed, which could easily be separated. The purified beef tallow was completely clear and dry and of a lighter color than the starting material. The soap residue content amounted to 0.030 weight-percent, the content of free fatty acids also to 0.030 weight-percent.

Example 19

4400 litres crude whale oil, hardened to 40° C., containing 0.32% free fatty acids, was treated. The crude, solid fat was continuously deacidified at 70° C. with 18.7 liters caustic soda solution consisting of 18% NaOH, to which 4% NaCl had been added. With these proportions, 0.5% soap was separated in single-phase form. The oil-soap mixture was introduced from the bottom into a reactor. After a time of stay of 20 minutes, the oil-soap mixture was passed continuously to a centrifuge. The sludge was removed from the centrifuge at periodic time intervals. The samples taken from time to time in front of the centrifuge showed a soap content of 0.56 to 0.64%. The corresponding samples taken at the same time behind the centrifuge were clear and had a soap content of 0.003 to 0.009% and were free of nickel. The consumption of caustic solution was less than in the previously customary deacidification processes.

Example 20

10,550 litres crude whale oil, hardened to 30° C., which still contained traces of nickel from the hardening and which had a content of 0.29% free fatty acids, was treated. The crude solid fat was deacidified, as in Example 19, with 40.6 liters caustic soda solution containing 18% NaOH and continuously passed from the bottom through a reactor having a useful content of 1000 liters, 9590.6 liters continuously overflowing into a centrifuge and being freed from the soap. The remaining 1000 liters flowed from the bottom over the centrifuge in order to empty the reactor. The rate of flow was kept variable. The sludge removal periods were so selected that the same quantities of dry soap were removed in each case from the sludge space. In this case also, the soap was obtained in single-phase form. The samples taken from time to time in front of the centrifuge showed a soap content of 0.52 to 0.58%. The corresponding samples taken at the same time behind the centrifuge were clean, of a lighter color and had a soap content of 0.003 to 0.009% and were free of nickel.

We claim:

1. Process for refining solid oils and fats by deacidification, which comprises gently stirring a molten mass of a solid fat having a solidification point of from 18 to 20° C., introducing at a temperature between about 30 and 100° C. drops of a sodium hydroxide solution having a minimum diameter of 0.2 mm. and a maximum diameter of 5 mm. through the surface and into the interior of said molten solid fat, so that at the time of passage through the surface of the drops of sodium hydroxide solution have a diameter as just set out in at least the stoichiometric quantity based on the free fatty acid content in said fat, controlling the rate of said stirring to effect the intimate mixing of said sodium hydroxide solution with said fat, regulating the quantity of water in said introduced sodium hydroxide solution so that the total amount of water present following the de-acidification does not exceed 1.5-fold weight of the soap formed, and centrifugally separating coarsely granular, single-phase structure, soap stock from the molten fat.

2. Process for refining solid oils and fats by deacidification, which comprises gently stirring a molten mass of a solid fat having a solidification point of from 18 to 20° C., introducing at a temperature between about 30 and 100° C. a stream of a sodium hydroxide solution having a minimum diameter of 0.2 mm. and a maximum diameter of 5 mm. through the surface and into the interior of said molten solid fat, so that at the time of passage through the surface of the stream of sodium hydroxide solution has a diameter as just set out in at least the stoichiometric quantity based on the free fatty acid content in said fat, controlling the rate of said stirring to effect the intimate mixing of said sodium hydroxide solution with said fat, regulating the quantity of water in said introduced sodium hydroxide solution so that the total amount of water present following the de-acidification does not exceed 1.5-fold weight of the soap formed, and centrifugally separating coarsely granular, single-phase structure, soap stock from the molten fat.

3. Process according to claim 1, in which said sodium hydroxide solution contains between about 8 and 40% by weight of sodium hydroxide.

4. Process according to claim 1, in which said contacting is effected under a pressure of at least atmospheric pressure.

5. Process according to claim 1, which said contacting is effected in the substantial absence of air.

6. Process according to claim 1, in which said contacting is effected in the presence of a chemical compound having an affinity for chemically binding water, which compound is inert with respect to the reactants and reaction products.

7. Process according to to claim 6, in which said chemical compound is sodium chloride.

8. Process according to claim 1, in which said contacting effected with a sodium hydroxide solution containing sodium chloride in an amount of about 4% by weight up to saturation.

9. Process according to claim 1, in which said sodium hydroxide solution is used in an amount which is from 100–500% greater than the amount stoichiometrically required for the neutralization of the free fatty acids present in said fat.

10. Process according to claim 1, which comprises continuously effecting the centrifugal separation of said formed soap from the reaction mixture containing the same and periodically removing the firmly pressed soap formed in said separation.

11. Process according to claim 2, which said sodium hydroxide solution contains between about 8 and 40% by weight of sodium hydroxide.

12. Process according to claim 2, in which said contacting is effected under a pressure of at least atmospheric pressure.

13. Process according to claim 2, in which said contacting is effected in the substantial absence of air.

14. Process according to claim 2, in which said contacting is effected in the presence of a chemical compound having an affinity for chemically binding water, which compound is inert with respect to the reactants and reaction products.

15. Process according to claim 14, in which said chemical compound is sodium chloride.

16. Process according to claim 2, in which said contacting is effected with a sodium hydroxide solution containing sodium chloride in an amount of about 4% by weight up to saturation.

17. Process according to claim 2, in which said sodium hydroxide solution is used in an amount which is from 100–500% greater than the amount stoichiometrically required for the neutralization of the free fatty acids present in said fat.

18. Process according to claim 2, which comprises continuously effecting the centrifugal separation of said formed soap from the reaction mixture containing the same and periodically removing the firmly pressed soap formed in said separation.

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