

- [54] **CLAY-HEAT REFINING PROCESS**
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Related U.S. Application Data

- [63] Continuation of Ser. No. 877,424, Nov. 17, 1969, abandoned.
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- [58] Field of Search **260/419, 423, 424, 429**

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[57] **ABSTRACT**

Crude fatty substances, including edible and inedible fats and oils and free fatty acids, are refined by heat treatment in the temperature range of about 250°–500°F in the presence of a bleaching adsorbent or in the presence of phosphoric acid and a bleaching adsorbent. This refining can be used in lieu of the conventional alkali-refining of fats and oils.

8 Claims, No Drawings

CLAY-HEAT REFINING PROCESS

This is a continuation, of application Ser. No. 877,424, filed Nov. 17, 1969 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the refining of crude fatty substances, such as, unrefined free fatty acids, fatty oils and fats, by the use of heat treatment of the fatty substances in the presence of a bleaching adsorbent and preferably also in the presence of a small amount of phosphoric acid. This process may be used in lieu of conventional alkali refining. It is applicable to the treatment of edible oils and fats for the production of margarine, shortening, salad and cooking oils, coating fats, etc. as well as for treatment of inedible products such as inedible tallow, fatty acids, and oils for the paint and resin industry. It may be combined with conventional bleaching and deodorizing operations and is adapted for combination with hydrogenation processes.

The processes most widely used for the refining of fats and oils at present are the well known alkali refining processes. Acid refining operations have been proposed but have not been favorably received by the industry. In alkali refining the free fatty acids are converted to soaps which are eventually removed from the oil in a water phase. The recovered oil is then bleached with an adsorbent, filtered and deodorized either before or after hydrogenation.

There are several disadvantages involved in the use of alkali refining. First of all there are the expensive installation costs of the equipment, particularly the centrifuges in which the aqueous phase is separated from the oil. Then there are other centrifuges in which the oil is washed with water to remove residual alkali and soap. These centrifuges run continuously and at times provide quite a maintenance problem. Another serious disadvantage of alkali refining is the seemingly inevitable amount of saponification of the oil by the action of the alkali, resulting in decreased oil yields.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a process for the refining of crude fatty substances without the use of alkali. The crude fatty substance is contacted with an adsorbent, which is preferably an acid-activated clay, at a temperature in the range of about 250°F to 500°F in the substantial absence of air, for a short time. This step is improved by carrying out the heat treatment process in the presence of a small amount of phosphoric acid, which has the effect of lowering the temperature of treatment and improving the quality of the product. After this treatment the adsorbent and impurities adsorbed thereon are removed by filtration. Treated oils and fats can be deodorized directly or hydrogenated prior to deodorization. Alternatively, a mixture of oil, adsorbent and acid without filtration and after addition of a suitable catalyst can be hydrogenated directly; the clay with adsorbent impurities and spent catalyst are then filtered off, and the filtered oil is finally deodorized. In the course of these deodorizations the volatiles including the free fatty acids are removed from the oil.

DETAILED DESCRIPTION

The process of the invention may be applied to a wide variety of oils including most of the usual edible oils and fats of commerce. The process can also be applied to inedible fatty materials such as inedible tallow,

fatty acids and crude oils for the paint industry. The fatty substances which have been successfully treated by the process include soybean oil, rapeseed oil, marine oil, sunflower seed oil, peanut oil, palm oil, palm kernel oil, coconut oil, lard, inedible tallow, and oleic acid.

Any of the commercial bleaching adsorbents may be used in the process but it has been found that the bleaching clays and especially acid-activated bleaching clays (e.g. Special-Filtrol) are significantly better than the other bleaching adsorbents. It has further been found that the acid-activated bleaching clay may be used either in freshly prepared form or in the form of a spent activated clay from other oil refinery processes. The clay is preferably used in an amount in the range of from about 0.1 to about 6% by weight based on the weight of the oil, depending upon the nature of the oil being processed. Thus, a relatively clean oil, such as palm kernel oil, may require only about 0.1 percent adsorbent, whereas corn oil may require, for example, about 6 percent. A small amount of filter aid, such as diatomaceous earth, may be added with the adsorbent to facilitate the eventual filtration. This is usually less than about 1.0 percent by weight based on the weight of the oil with 0.5 percent being quite satisfactory. Diatomaceous earths have no adsorbent properties and are used solely for improving filtration. Where the adsorbent is used without pre-addition of phosphoric acid the temperature of treatment is usually in the range of from about 400°-500°F. Satisfactory treatment of edible oils with acid-activated clay alone has been attained at about 450°F.

The phosphoric acid is employed in an amount which may vary from about 0.1 percent to 1.0 percent. Again, the amount of phosphoric acid depends to some extent upon the nature of the oil being treated. The amount of phosphoric acid also depends to some extent upon the temperature at which the oil is to be processed. Lower treating temperatures can be used where more phosphoric acid is used in the pre-treatment stage. The preferred temperature at which the oil is heated in the presence of the adsorbent clay is about 325°-350°F where a pre-treatment with about 0.1 percent H_3PO_4 has been carried out. The phosphoric acid may be mixed with the oil or fat at any temperature at which the oil or fat is in liquid condition. Preferably a short pre-treatment of the oil or fat with phosphoric acid is effected by agitating the acid with the oil or fat at a temperature ranging from about room temperature to about 100°F following which the adsorbent clay is added and the mixture of oil, acid and adsorbent is then heated to a temperature in the desired higher range. The pretreatment of the oil with phosphoric acid at the relatively low temperature prevents foaming during heating of the oil.

The time of the treatment is relatively short, normally requiring only that the fatty substance be thoroughly contacted with the treating agent at the maximum temperature involved. Where bleaching adsorbent is used alone it may be added to the fatty substance prior to heating and the fatty substance and adsorbent are then heated together, under vacuum or inert atmosphere, to the maximum temperature, e.g. 450°F, followed by immediate cooling and filtering. It will be understood, however, that the adsorbent can also be added to pre-heated fatty substance or to the fatty substance at any heating stage. Where phosphoric acid is employed it is preferred that it be added at relatively low temperature

as described above and contacted with the fatty substance for a short period of time, e.g. about 10 to 30 minutes prior to adding the adsorbent and heating to maximum treating temperature. Alternatively the phosphoric acid and adsorbent may be added together to the oil prior to heating or at any heating stage.

The use of vacuum during the heating is ordinarily for the purpose of excluding air. However, the process may be combined with steam stripping while drawing a vacuum so as to remove free fatty acids and other volatiles. Alternatively, the heat treatment can be conducted under an atmosphere of inert gas, e.g. nitrogen.

REPRESENTATIVE EXAMPLES

EXAMPLES 1-11

Various crude fatty substances which normally would be processed by alkali-refining were subjected to combined phosphoric acid and acid-activated clay heat treatment. A 1,000 gram sample of each crude oil was placed in a 2,000 ml. threeneck distillation flask fitted with a thermometer, a variable speed agitator and a glass tube connected to a nitrogen supply. The oil was heated to 100°F. The phosphoric acid was pipetted into the flask, then the oil-acid mixture stirred at slow speed for 15 minutes. The adsorbent (Special-Filtrol) and filter-aid (Celite) were added and a stream of nitrogen started into the flask to exclude air and carry-off moisture released during heating. Heat was applied until the desired treatment temperature was reached. Also, the upper portion of the flask was kept warm to prevent moisture condensation. As soon as the desired reaction temperature was reached, the heating was stopped and the flask cooled to 230°F. The oils were filtered at this temperature through a Buchner funnel.

The clay-heat refined oils were analysed for color, FFA, and loss and then deodorized under conventional conditions. Table I lists the results for each oil.

cent) was placed in a closed vessel which was equipped with steam and water coils, electric booster heater, agitator and ejector for drawing vacuum. 200 Grams of phosphoric acid was added to the oil and the mixture was agitated for 30 minutes at room temperature (80°F). 8 Lb. of activated clay (Special Filtrol No. 4) and 2 lb. of filter-aid (Celite No. 545) were added, the vessel closed and a vacuum to about 19 inches Hg abs. pressure drawn. The batch was heated to the reaction temperature (from 80°F to 350°F) in 45 minutes. Without hold-up time at 350°F, the batch was cooled to 230°F and the clay and filter-aid removed using a plate and frame filter. Laboratory deodorizing produced bland oil; also, the clay-heat refined oil hydrogenated from a Zeiss refractive index of 79.3 to 62.3 in 40 minutes. Both test results denote satisfactory performance.

EXAMPLE 13

An 18,500 lb. batch of crude soybean oil (FFA-0.33 percent) was run into a batch hydrogenation vessel of the type used in the edible oil industry. 35 Lbs. of concentrated H_3PO_4 (0.19 percent) was added at 100°F and the oil and acid were agitated at this temperature for 20 minutes at atmospheric pressure. 300 Lbs. (1.6 percent) of acid-activated clay (Special-Filtrol No. 4) was added and the mixture heated to 345°F under a vacuum (6-12 inches Hg absolute pressure) with 30 minutes heating time from 325°F to 345°F. A sample of the oil at this point showed a colour of 0.4 R/5Y and a free fatty acid content (FFA) of 0.66 percent. Hydrogenation catalyst was then added to the batch of oil at 345°F and the oil was hydrogenated directly in the presence of the refining agents and catalyst. The hydrogenated oil (RI 60°C - 1.4561) was cooled to 210°F, filtered bleached and deodorized to provide a product oil

TABLE I

Analyses	H ₃ PO ₄ -CLAY-HEAT REFINING OF A VARIETY OF CRUDE OILS										
	Examples of Crude Fatty Substances										
	1	2	3	4	5	6	7	8	9	10	11
	Soybean	Expeller Rapeseed	Sun-flower	Corn	Peanut	Palm	Coconut	Palm Kernel I	Palm Kernel II	Seal	Dry Rened-ered Lard
Crude FFA (%)	0.30	0.31	0.28	2.35	1.07	3.55	1.23	5.60	6.40	1.46	** 0.34
Treatment:											
Active Clay (%)	2.0	4.0	1.5	6.0	4.0	4.0	2.0	0.1	2.0	4.0	2.0
Filter-Aid (%)	0.5	1.0	0.4	1.5	1.0	1.0	0.5	0.025	0.5	1.0	0.5
Phosphoric Acid (%)	0.1	0.4	0.2	1.0	0.2	0.4	0.1	0.02	0.1	0.2	0.3
Temperature (°F)	350	350	350	350	350	350	350	350	350	350	350
Treated Oil Color (Red)	1.0	1.3	0.4	2.0	0.9	1.4	0.4	1.2***	0.7	—	0.5
FFA (%)	0.73	0.36	0.45	2.67	1.28	3.89	1.53	5.7	7.3	—	0.48
Deodorized											
Oil Color (Red)	0.7	1.0	0.4	2.0	0.7	1.7	0.7	0.5	0.7	1.3	0.6
FFA (%)	0.03	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.03	0.03	0.03
Flavour	Bland	Good	Bland	Bland	Bland	Bland	Bland	Bland	Bland	Bland	Bland
AOM (hr)	6	18	9	13	18	60	60	60	60	25	4
Schaal (days)	11	12	15	8	17	15	30	11	20	8	5

* Directly hydrogenated to 76 IV

** Crude oil colour very poor (9.0R)

*** Bleached with 0.5% clay to obtain a color below 1.0R

The clay-heat treatment satisfactorily refined all types of crude oil listed in Table I. Deodorized oil color, FFA, flavour, and stability, measured by AOM and Schaal-oven, indicated that these oils are equal to oil produced using caustic refining.

EXAMPLE 12

A 400 lb. batch of crude soybean oil (FFA-0.30 per-

cent) of a quality substantially equivalent to that obtained by caustic refining, hydrogenating, bleaching and deodorizing.

EXAMPLE 14

Samples of crude and caustic refined soybean oil were obtained during a plant alkali-refining operation. The crude sample was subjected to H₃PO₄-clay-heat re-

fining using 0.2 percent H_3PO_4 and 2 percent Special Filtrol No. 4 with the maximum heat-treatment being at 360°F. The caustic refined sample was bleached with 1 percent Special Filtrol No. 4. Both the caustic refined, bleached oil and the H_3PO_4 -clay-heat refined oil were deodorized for 2 hours at 485°F using 1 percent/hr. of stripping steam. Stability tests on the deodorized oils were run without antioxidants or citric acid. The results of the comparison are summarized in Table II.

TABLE II

Analysis	Caustic Refining - Clay-Heat Refining Comparison Plant Caustic Refined Oil				H_3PO_4 -Clay-Heat Refined Oil	
	Crude Oil	Refined	Refined and Bleached	Deodorized	Refined	Deodorized
Free Fatty Acid	0.68%	0.03%	0.04%	0.02%	0.90%	0.02%
Color (Lovibond)	—	9.5R	1.8R	0.6R	1.1R	0.8R
Peroxide Value mc/kg	3.0	3.5	2.0	Nil	Nil	Nil
AOM (70 mc/kg) Stability		6 hr	6 hr	10 hr	12½ hr	12 hr
Schaal Oven Stability				14 days		13 days
Brown Bottle Stability				5 weeks		7 weeks
Tocopherols	0.1475%	0.1384%	0.1255%	0.0505%	0.1361%	0.0914%
Free Phosphoric Acid	Nil	Nil	Nil	Nil	trace	Nil
Conjugation						
E-Value at 233 m μ	3.1	2.9	3.0	7.0	5.3	9.6
E-Value at 268 m μ	0.31	0.26	1.7	1.5	2.0	1.7
Conj Diene (%)	0	0	0	0.58	0	0.81
Conj Triene (%)	0.003	0.002	0.043	0	0.054	0

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From Table II it will be seen that the product oils from the two refining processes were of substantially equal quality.

EXAMPLE 15

Crude soybean oil was heated to approximately 350°F in the presence of 2% of acid-activated clay (Special Filtrol No. 4) and 0.2 percent H_3PO_4 was added at this maximum treating temperature. After thorough agitation of the treated oil, it was cooled and filtered. The product quality was about the same as when the H_3PO_4 was added at 100°F. However, less foaming occurred during heating when the acid was added at the lower temperature.

EXAMPLE 16

Two samples of inedible tallow, analyzing FAC colour 19 and FFA-2.2 percent, were obtained. One sample was bleached by a normal bleaching process with 2.0 percent Special Filtrol No. 4 for 15 minutes at 240°F. The bleached product had a Lovibond Colour (5¼ inches) of 60y-8.0R-0.8B and an FAC colour of 9. The other sample was subjected to H_3PO_4 -clay-heat refining in the presence of 2.0 percent Special Filtrol No. 4 and 0.2 percent H_3PO_4 at a maximum temperature of 360°F. The filtered product had a Lovibond Colour

(5½ inches) of 15Y-1.0R and a FAC colour of 1 and was suitable for use as a toilet soap base. The H_3PO_4 -clay-heat refining had far greater colour removal power than the normal bleaching process.

EXAMPLE 17

Three samples of a No. 2 inedible tallow were obtained. This crude material had an FAC colour of 31 and a FFA of 20.0 percent. The samples were subjected to H_3PO_4 -clay-heat refining with different amounts of

clay and acid. The results are given in Table III below:

TABLE III

Special Filtrol No. 4	H_3PO_4	Final FFA	Lovibond Colour (1") (5¼")		FAC Colour
2.0%	1.0%	20.4%	40Y-3.5R	50Y-16.0R	11
4.0%	2.0%	22.8%	15Y-1.1R	50Y-6.5R	5
6.0%	2.0%	22.6%	7Y-0.7R	50Y-4.5R	3

H_3PO_4 -clay-heat refining of No. 2 Tallow results in very much lighter colours than those obtained in bleaching. It is possible to upgrade No. 2 Tallow by this process to a material which approaches Bleachable Tallow after caustic refining and bleaching. This is not possible with present methods. Caustic refining cannot be done since the FFA of this material is too high, and bleaching is not effective enough.

EXAMPLE 18

A sample of single-distilled oleic acid was H_3PO_4 -clay-heat refined using various clay and acid levels. A heat test (heating the oleic acid to 200°C for 30 minutes) was used to evaluate heat stability. Results of these tests are summarized in Table IV.

TABLE IV

Special Filtrol No. 4	H_3PO_4 -Clay-Heat Refined (at 360°F) Colour				Heat Test Colour	
	H_3PO_4	Lovibond 5¼"	Gardner	Lovibond 1"	Gardner	
Control —	—	15Y-1.4R	3-4	40Y-4.2R	9-10	
2%	0.2%	17Y-1.1R	3-4	15Y-1.8R	7-8	
4%	0.2%	12Y-1.0R	3	14Y-1.4R	7	
4%	0.1%	15Y-1.1R	4	13Y-1.3R	7-8	

EXAMPLE 19 SOYBEAN OIL FOR PAINT AND RESIN MANUFACTURE

At present, caustic refined, heavily bleached SB oil is supplied for this purpose. The oil must be very light in colour after bleaching and also after heat-testing. Table V gives data on a H_3PO_4 -clay-heat refined SB oil for comparison to a representative set of specifications of an industrial SB oil user.

TABLE V

	Crude	Clay-Heat Refined (2% clay, 0.2% H_3PO_4 at 325°F)	Spec
Color (Gardner)	9	1	4
Color after heat test*	4 (ppt)	2	2
Unsaponifiable Matter**	0.57%	0.44%	—

*Heat test: 50 g of oil are heated to 500°F and held at this temperature 5 minutes.

**AOC'S Method Tk 1a-64T.

Clay-heat refined SB oil meets colour specifications before and after heat testing.

EXAMPLE 20

Three samples of crude East Coast Herring Oil were heated in a closed container in the presence of a small amount of a neutral bleaching clay (Pembina No. 75) under a blanket of nitrogen. After the maximum treating temperature was reached the samples were cooled to 350°F, a hydrogenation catalyst and filter aid were added and the samples were hydrogenated to an end point of 54.4 ZRI. The hydrogenated oil was then filtered, bleached and deodorized. The results are tabulated in Table VI below:

TABLE VI

TEST NUMBER	CLAY HEAT TREATMENT AND HYDROGENATION OF CRUDE EC HERRING OIL		
	1	2	3
Crude FFA	0.86%	0.87%	0.87%
Crude Color (Lovibond)	8.5 R	20.0 R	20.0 R
Neutral Clay Treatment	¼%	½%	½%
Maximum treatment temperature	500°F	500°F	450°F
Hydrogenation temperature	350°F	350°F	350°F
Hydrogenation time (minutes)	60	120	160
SFI at 21.1°C	—	28.6	20.6
Color after hydrogenation	light brown	brownish-red	brownish-red
Active clay used to bleach hydrogenated oil	½%	1%	2%
Bleached color (Lovibond)	1.8 R	2.8 R	1.1 R
Bleached FFA	1.02%	0.91%	0.94%
Deodorized color (Lovibond)	—	3.0 R 1.0 blue	0.5 R
Schaal Oven stability	—	9 days	12 days

From the above data it is shown that crude East Coast herring oil can be successfully processed by clay-heat refining to a hydrogenated, deodorized oil. Oil colour and flavour stability are both comparable to East Coast herring oil refined in the conventional manner.

EXAMPLE 21

For comparative purposes two samples of crude soybean oil were processed, one by heating to 450°F in the presence of acid-activated clay without H_3PO_4 and the

other by heating to 340°F in the presence of acid-activated clay and H_3PO_4 . In both tests 1.0 percent activated clay and 0.5% filter aid were used. In the test at 340°F, 0.1 percent H_3PO_4 was added to the crude oil prior to heating and the addition of the clay. The samples were cooled to 200°F and filtered, then bleached and deodorized. The results are given in Table VII, below:

TABLE VII

	CRUDE SOYBEAN OIL ACID-CLAY-HEAT TREATED	
	Treated at 450°F (no acid)	Treated at 340°F (plus H_3PO_4)
Crude Free Fatty Acid (FFA)	0.37%	0.37%
Treated FFA (FFA + H_3PO_4)	0.71%	0.54%
Color	1.1 R	1.8 R
Loss	1.50%	1.45%
Bleached FFA	0.71%	0.53%
Color	1.1 R	1.6 R
Deodorized FFA	0.02%	0.02%
Color	0.5 R	0.6 R
Flavour	bland	bland
Schaal-oven stability	7 days	7 days
Cold test	24 hours	23 hours

The above two tests show that with respect to crude soybean oil, equivalent results can be obtained by using either clay alone plus heating to about 450°F or phosphoric acid and clay plus heating to only 340°F. The treated oil can be hydrogenated.

EXAMPLE 22 H_3PO_4 -CLAY-HEAT REFINING COMBINED WITH STEAM REFINING TO REDUCE FFA'S (FREE FATTY ACIDS)

Crude palm kernel oil (800 g), FFA 6.4 percent was

pretreated with 0.1 percent H_3PO_4 . Activated clay (2percent) and filter aid (0.5 percent) were then added. The mixture was then heated to 420°F under vacuum. Agitation was provided by stripping the mixture with 1 percent H_2O per hour. Steam stripping was continued at 420°F for 1 hour, the charge was then cooled to 230°F and filtered. The filtered oil contained 0.84 percent FFA; its colour was 1.6R.

It will be seen from Example 22 that the H_3PO_4 -clay-heat refining operation may be satisfactorily combined

with steam stripping to provide a refined product of reduced free fatty acid content. This process is especially applicable to treatment of oils which have high FFA content and which are to be hydrogenated. The free fatty acids which may interfere with hydrogenation are reduced at the same time that color bodies and other impurities are being removed.

It will be seen that the process of the invention is capable of many adaptations and variations without departing from the spirit and scope thereof.

In the foregoing specification and ensuing claims all percentages, unless otherwise specified, are given in percent by weight based on the weight of the fatty substance being treated.

I claim:

1. A process for refining crude fatty substances selected from the group consisting of unrefined vegetable oils and fatty acids which comprises heating said crude fatty substances under vacuum or inert atmosphere in the presence of about 0.1 to 1.0 percent of phosphoric acid and about 0.1 to 6.0 percent of acid activated clay to a temperature of from about 325° to 500°F and then filtering the resulting product.

2. The process of claim 1 wherein the crude fatty substances are selected from the group consisting of oleic

acid, soybean oil, rapeseed oil, sunflower seed oil, peanut oil, palm kernel oil, coconut oil and corn oil.

3. The process of claim 1 wherein the fatty substance is pretreated with the phosphoric acid at a temperature up to about 100°F prior to adding the bleaching adsorbent and heating to a temperature in said range.

4. The process of claim 1 wherein the fatty substance is pretreated with about 0.1 percent phosphoric acid, the bleaching clay is added and the mixture is heated to about 325° to 350°F in the substantial absence of air.

5. The process of claim 1 wherein the crude fatty substance is a vegetable oil and the hot treated oil is subjected to hydrogenation.

6. The process of claim 5 wherein the hot treated oil is directly subjected to hydrogenation prior to filtering.

7. The process of claim 1 wherein the crude fatty substance is an unrefined vegetable oil and wherein the hot treated oil is steam-stripped during the heat treatment to remove free fatty acids.

8. A process for upgrading crude oleic acid consisting essentially of heat treating said crude acid in the presence of from about 0.1 to 1.0 percent of phosphoric acid and from about 0.5 to 6 percent of acid-activated clay at a temperature in the range of about 325°-375°F.

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