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DRY MODIFIED, ACID ACTIVATED BLEACHING EARTH, PROCESS OF
PRODUCTION AND USE THEREOF

Description

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The invention relates to a process for producing a bleaching earth, especially a dry-modified bleaching earth, to a bleaching earth obtained by the process, and to the use thereof for bleaching of vegetable or animal crude oil.

10 In the industrial production of oils and fats, bleaching earths are used to remove turbidity and discoloration, or else to remove oxidation accelerators. The adsorptive cleaning can significantly improve flavor, color and storage stability of the oils and fats. Cleaning is accomplished using various classes of bleaching earths.

15 A first group is the class of the highly active bleaching earths that are usually based on montmorillonite (HPBE = high-performance bleaching earth). This group especially includes acid-activated montmorillonites, wherein the acid activation is conducted in a complex process by dealumination of the raw clays with concentrated acids at high temperatures. This process affords a bleaching earth product with a very high specific
20 surface area and large pore volume. Even the use of small amounts of this high-performance bleaching earth leads to noticeable cleaning of the crude oils. Small use amounts in the bleaching process are desirable because the spent bleaching earth firstly binds residual amounts of oil, which reduces the yield, and the spent bleaching earth secondly has to be disposed of in accordance with applicable regulations.

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A disadvantage of these high-performance bleaching earths is the fact that the dealumination with acid causes large amounts of acidic salt-rich wastewater to occur during the production, and this can be processed or disposed of only in costly and inconvenient processes. The high costs for the disposal of the wastes and the complex
30 production process are the reasons for the comparatively high costs of such high-performance bleaching earths.

A further group is the class of naturally active clays. These naturally occurring bleaching earths have already been used for hundreds of years for the cleaning of fats and oils. These naturally active systems (also called fuller's earth) can be provided very inexpensively. However, they have only low bleaching power, and so they are usually unsuitable for the cleaning of oils and fats that are difficult to bleach. Moreover, by comparison with high-performance bleaching earths, significantly greater amounts of the adsorbent have to be used in order to achieve the desired bleaching result. As a result, however, higher losses of oil or fat have to be accepted, since the bleaching earths cannot be separated in pure form, and certain amounts of oil or fat remain in the bleaching earth.

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The third class of bleaching earths, called surface-activated systems (SMBE = surface-modified bleaching earth; surface-activated bleaching earths), represents a compromise between low production costs and acceptable activity. Here, a naturally active raw clay is contacted with small amounts of acid and hence "in situ activation" is achieved. For this process, raw clays comprising attapulgite and hormite have been found to be especially useful. These have quite a high specific surface area for natural raw clays of about 100 to 180 m²/g and a pore volume of about 0.2 to 0.35 mL/g. Since, however, salts formed in the acid activation or unreacted fractions of the acids are not washed out, these remain on the product and are at least partly also deposited in the pores. As a result, these acid-activated bleaching earths generally do not attain the same efficiency as that obtained by high-performance bleaching earths (HPBE) which are produced by dealumination with acid. However, the simple production process enables comparatively inexpensive production, since no acidic wastewater is obtained.

WO 96/33621 discloses the production of bleaching earths from clay material having a water content of not more than 8% by weight by grinding the clay with solid organic polycarboxylic acids.

WO 99/02256 describes the production of bleaching earths from clay material, wherein the clay is first preferably dried to a water content of 8% to 10% by weight, then activated with a concentrated solution of an inorganic or organic acid and subsequently dried to a maximum water content of 13% by weight.

A common factor among the abovementioned bleaching earth types is that, after activation or prior to use, they are dried to a minimum water content (usually 8% to 12% by weight, typically 10% by weight or less).

- 5 The main field of use of the bleaching earths is the refining of oils and fats, in this case the bleaching of course. After the bleaching, the refined oil is expected to meet particular demands in relation to color, flavor and shelf life. For instance, the oil must not be too dark and, according to the oil type, may have a yellow to green hue. In addition, the oil is to have a long shelf life without any deterioration in flavor, i.e. is not to have a rancid
10 taste.

In the processing which is customary nowadays, the oil, after pressing, is first degassed and dried in order to remove dissolved oxygen, for example. Subsequently, gums, especially phospholipids, are removed. For this purpose, the dried and degassed oil is
15 admixed with phosphoric acid and stirred at about 95°C and standard pressure for about 15 to 20 minutes. In order to be able to remove the gums more easily, toward the end of the degumming, further water is added, for instance in a proportion of 0.2% by weight. After stirring briefly, the lecithin phase is removed, for example by centrifuging. The subsequent bleaching of the degummed oil comprises two stages, a wet bleaching stage
20 and a vacuum bleaching stage. For the wet bleaching, the degummed oil is admixed with 0.1% to 0.5% by weight of water and, after the oil has been heated to 95°C, 0.3% to 2% by weight of bleaching earth is added. The mixture is then stirred at standard pressure for about 20 minutes. Subsequently, vacuum is applied (for example 100 mbar) and the oil is stirred at 95°C for a further 30 minutes. After the bleaching, the spent bleaching
25 earth is removed, for example by filtering the mixture through a suction filter covered with a paper filter.

After the bleaching, the oil is deodorized. For this purpose, superheated steam having an exit temperature of, for instance, 200 to 240°C is passed through the oil in order to
30 remove free fatty acids and unpleasant flavoring and odorous substances. The deodorization is conducted under reduced pressure at a pressure in the region of less than 5 mbar, preferably 1 to 3 mbar, and in some cases also lower.

After the refining, the oil has to meet particular demands in relation, for example, to color, taste and shelf life. For example, the oil should not have a brown appearance, but a yellow to green hue according to the type. One standard for this purpose is the Lovibond red color value (CV red), which should be at a minimum. In order to increase shelf life, the oil should have a very low iron or phosphorus content. Moreover, the oil should be of minimum sensitivity to oxidation, in order to prevent the development of a rancid odor and taste.

As well as the high quality of the oil, the refining, however, should also be conducted in a rational and inexpensive manner. The process outlined above has become established in commercial oil processing. However, there is still a need for optimization of oil refining, such that it can be conducted more quickly and at lower cost without having to accept losses in the quality of the oil.

The raw clays known from EP 1893329 B1 or EP 2099561 B1 are a good starting material for high-quality bleaching earths. To date, these have been used to produce high-quality SMBEs after reaction with 3% sulfuric acid and drying to a water content of 10% by weight. A disadvantage of the production of these SMBEs is that the raw clay has a water content of about 60% by weight and is transported with this high water content. The water content is then reduced to 10% by weight in production by heating and driving out the water. This is costly and not environmentally sustainable.

It was an object of the invention to develop an efficient bleaching earth that does not have these disadvantages.

It was a particular object of the invention to provide a process for producing an adsorbent, especially a bleaching earth, which avoids the disadvantages of the prior art and leads to a product having high adsorption capacity, especially with regard to the bleaching effect of oils and fats.

This object is achieved by a process having the features of Claim 1. Advantageous developments of the process are the subject of the dependent claims.

The invention firstly provides a process for producing a dry-modified bleaching earth, wherein a water-rich raw clay is first dried to a reduced water content, and the raw clay having a reduced water content is mixed and ground with 1%-5% by weight (based on the weight of the raw clay) of a solid organic and/or concentrated inorganic acid. It is a feature of the process of the invention that the bleaching earth thus obtained has a water content of 20% to 40% by weight. In the production of the bleaching earth of the invention, it is consequently possible to dispense with a drying step after the grinding of the raw clay with the solid organic and/or concentrated inorganic acid, which makes the production inexpensive and less labor-intensive overall than in conventional processes. The bleaching earths obtainable by the process of the invention nevertheless show excellent results in the bleaching fats or oils, as shown in the experimental examples.

Since the process of the invention includes only moderate drying of the raw clay, it is advantageously possible to resort to mild drying methods that do not entail any great technical complexity or energy consumption. More particularly, it has been found that the raw clay can be sun-dried in order to reduce the water content from originally 50% to 70% by weight down to 20% to 40% by weight. The residual water content to be attained is partly determined by the duration of the solar drying, which is typically 1 to 14 days, preferably less than 1 week and ideally 2 to 4 days (depending on the duration and intensity of sunshine). Such solar drying increases the effective proportion of solid constituents in the raw clay, such that less water is ultimately transported for the same mass and hence the transport costs (based on the solid constituent of the raw clay) are reduced.

The water-rich raw clay preferably has a water content of 50% to 70% by weight. However, the process of the invention can also be used advantageously for raw clays having other water contents, for example for water contents of more than 40% by weight.

After the drying and activation with solid organic and/or concentrated inorganic acid, the bleaching earth ideally has a water content of 30% to 40% by weight. However, water contents down to about 20% by weight are likewise possible in accordance with the invention. The advantage of the gentle drying of the raw clays achievable in accordance with the invention and the omission of a drying step after the grinding of the

raw clay with the solid organic and/or concentrated inorganic acid can, however, best be realized when the raw clays are dried to the preferred water content range of 30% to 40% by weight.

- 5 The process of the invention advantageously works with solid organic acids selected from the group comprising citric acid, malic acid and tartaric acid, and/or concentrated inorganic acids such as, in particular, concentrated sulfuric acid and/or concentrated phosphoric acid. The acids may be present alone or in any desired mixtures with one another. Tartaric acid has surprisingly been found to be particularly effective in the
10 bleaching of vegetable oil, especially of rapeseed oil.

The proportion of solid organic and/or concentrated inorganic acid is typically in the range of 1%-5% by weight (based on the weight of the raw clay), and a proportion of 1%-3% by weight has been found to be preferable.

15

The water-rich raw clay which is particularly suitable for the process of the invention contains a mixed smectite-silica gel phase. Particular preference is given to raw clays as described in detail in EP 1893329 B1 and EP 2099561 B1. Explicit reference is made here to the raw clays described in these two documents and the characterization and
20 properties thereof, and likewise to the experimental details for the determination of the chemical and physical properties.

- The invention further provides a bleaching earth, especially a dry-modified bleaching earth (DMBE for short) obtainable by the process described in detail above, wherein the
25 water-rich raw clay comprises a mixed smectite-silica gel phase. By contrast with bleaching earths according to prior art, the bleaching earth of the invention has a comparatively high water content. While bleaching earths are dried in a costly and inconvenient manner to a water content of about 10% by weight in the prior art, the bleaching earths of the invention have water contents of 20% by weight or more,
30 typically up to 40% by weight. Surprisingly, bleaching earths having such high water contents can be ground without any problem to typical bleaching earth particle sizes (dry sieve residue on 63 μm sieve: 20% to 40% by weight; dry sieve residue on 25 μm sieve: 40% to 65% by weight) without sticking of the grinders.

The invention further provides for the use of the (especially dry-modified) bleaching earth of the invention for refining of fats and/or oils, especially of vegetable fats and/or oils. The refining preferably comprises the bleaching and optionally the subsequent
5 deodorization, followed by the removal of the bleaching earth, especially by filtration.

The invention also finally provides a method of refining fats and/or oils. This involves providing a crude oil obtained from vegetable or animal material. The crude oil is subjected to bleaching by treating it with an (especially dry-modified) bleaching earth
10 of the invention. The bleached oil is then separated from the bleaching earth, for example by filtration.

A suitable starting material for the process of the invention for production of a dry-modified bleaching earth in particular, i.e. in the form of a water-rich raw clay, is
15 especially a mixed smectite-silica gel phase that features a very high specific surface area of more than 120 m²/g, preferably more than 150 m²/g. The mixed smectite-silica gel phase may have a specific surface area of up to 300 m²/g, preferably up to 280 m²/g. In addition, the mixed smectite-silica gel phase features a very high total pore volume of more than 0.35 mL/g. The mixed smectite-silica gel phase has an unusually high
20 proportion of a silica gel phase and therefore has a high silicon content, calculated as SiO₂, of at least 60% by weight, preferably more than 63% by weight, especially preferably more than 70% by weight. In accordance with one embodiment of the invention, the silicon content of the mixed smectite-silica gel phase is less than 85% by weight. In a further embodiment, the silicon content of the mixed smectite-silica gel
25 phase, calculated as SiO₂, is less than 75% by weight. Such water-rich raw clays that are suitable in accordance with the invention are known from Sohling et al., Clay Minerals (2009) 44, 525-537 and Emmerich et al., Clay Minerals (2010) 45, 477-488.

Especially suitable for the process of the invention for production of dry-modified
30 bleaching earths in particular are raw clays as described in detail in EP 1893329 B1 and EP 2099561 B1. Explicit reference is made here to the raw clays described in these two documents and the characterization and properties thereof, and likewise to the experimental details for the determination of the chemical and physical properties.

Surprisingly, it is possible to use the sun-dried raw clay to produce a bleaching earth that does not need a further drying step, i.e. is capable of effectively bleaching fats and oils at a water content of 20%-40%. This was not to be expected according to the current
5 state of the art.

EXAMPLES

The invention is elucidated in detail hereinafter by examples.
10

The following analysis methods and general production and test methods were employed:

Oil analysis:
15

The color values in oils (Lovibond color values) were determined in accordance with AOCS Cc 13b-45. The chlorophyll A determination was effected in accordance with AOCS Cc 13d-55.

20 Activation of the raw clay with sulfuric acid (state of the art, for comparative purposes):
The raw clay is mixed with water and then activated with 3% by weight of H₂SO₄. For this purpose, 100 g of raw clay powder dried to about 10% H₂O are mixed intimately with 208 g of water and 2.83 g of H₂SO₄ (96%) in a beaker. The resultant mixture is dried at 110°C to a water content of about 10% and then ground to a typical bleaching
25 earth fineness (dry sieve residue on 63 µm sieve: 20% to 40% by weight; dry sieve residue on 25 µm sieve: 40% to 65% by weight).

Inventive activation of the raw clay with solid organic or concentrated inorganic acid:
The raw clay is – unless stated otherwise in the examples – first dried to a water content
30 of about 35% by weight, then mixed intimately with 3% by weight of solid organic or concentrated inorganic acid and hence activated. Subsequently, the mixture is ground to a typical bleaching earth fineness (dry sieve residue on 63 µm sieve: 20% to 40% by weight; dry sieve residue on 25 µm sieve: 40% to 65% by weight).

Bleaching of vegetable oil

An optionally degummed and deacidified vegetable oil is – according to the oil used –
 5 bleached with 0.30%-1.60% by weight of bleaching earth at 100-120°C under a pressure
 of 30-100 mbar for 20-30 minutes. Subsequently, the bleaching earth is filtered off and
 the color values of the oil (CV red) are determined with the aid of the Lovibond method
 in a 5¼” cuvette (unless stated otherwise). A portion of this oil is additionally deodorized
 by steam treatment (30 minutes, at 220-270°C, < 1 mbar). The oil obtained here is also
 10 analyzed with the aid of the Lovibond method. The values after the deodorization are of
 particular relevance here, since almost all oils in practice are deodorized after bleaching.

Example 1: Bleaching earth made from sun-dried raw clay for bleaching of rapeseed oil

15 A raw clay which has been sun-dried to a water content of 21.5% or 26.2% or 27.6% (in
 accordance with EP 1893392 B1) was homogenized with 3% by weight of citric acid in
 each case, dried to about 10% by weight of water and ground, in order to obtain 3
 specimens of a bleaching earth. Rapeseed oil was bleached with 3 specimens of the
 above-described bleaching earth and, for comparison, with a high-quality SMBE
 20 (Tonsil® Supreme 112 FF, Clariant Produkte (Deutschland) GmbH). For this purpose,
 a degummed and deacidified rapeseed oil was bleached with 0.60% by weight of
 bleaching earth under a pressure of 30 mbar at 110°C for 30 minutes. Subsequently, the
 bleaching earth was filtered off and the color values (CV) of the oil were determined
 with the aid of the Lovibond method in a 5¼” cuvette. A portion of this oil was
 25 additionally deodorized by steam treatment (30 minutes, 230°C, < 1 mbar). The oil
 obtained here was also analyzed with the aid of the Lovibond method.

Table 1 shows the results of the bleaching operations.

Table 1		
Bleaching of rapeseed oil		
Sample	Bleaching	Deodorization

	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF	1.4	0.03	0.6	0.04
Specimen 1.1 (26.2% by wt. of water, dried to 10% by wt.)	6.0	0.02	0.3	0.018
Specimen 1.2 (21.5% by wt. of water, dried to 10% by wt.)	5.8	0.01	0.3	0.016
Specimen 1.3 (27.6% by wt. of water, dried to 10% by wt.)	4.6	0.01	0.3	0.018

The bleaching earths activated with solid citric acid attain moderate red values on bleaching of rapeseed oil (CV red 6.0-4.6 according to Lovibond AF 995), but excellent red values after deodorization (CV red 0.3) and very good chlorophyll removal (< 0.02 ppm). This example shows that solar drying does not damage the raw clay and good bleaching earths (specimens 1.1 to 1.3 as comparative specimen) are producible therewith.

Example 2: Filtration characteristics and bleaching of palm oil with sun-dried raw clay

3 specimens of raw clay sun-dried to a water content of about 35% by weight (in accordance with EP 1893392 B1) were divided and half of each was dried at 110°C to a water content of about 9% by weight. The water-containing and dried specimens were analyzed separately with respect to their filtration times. For this purpose, 10 g in each case of the raw clay specimen are added to 100 g of crude linseed oil and stirred at 96.5°C for 10 min. The raw clay-linseed oil mixture is then filtered through a suction filter and the time taken for the entire visible surface of the filtercake (essentially raw clay) to be visually dry is recorded. Table 2 shows the results.

Table 2		
Filtration characteristics		
Sample	Water content (% by wt.)	Filtration time (s)

Specimen 2.1 (inventive)	32.3	51
Specimen 2.1 (comparative specimen)	9.0	73
Specimen 2.2 (inventive)	34.8	50
Specimen 2.2 (comparative specimen)	8.9	65
Specimen 2.3 (inventive)	36.8	50
Specimen 2.3 (comparative specimen)	9.0	64

It was found that the materials which have only been sun-dried had better (i.e. shorter) filtration times than the materials dried conventionally to a lower water content, and consequently the separation of the bleaching earth from the oil in the case of sun-dried materials is improved.

Table 3 shows the results for CV red after bleaching and deodorization of palm oil for bleaching earth specimen 2.2 (moist with 34.8% water, dry with 8.9% water) compared to an SMBE (Tonsil® Supreme 112 FF, Clariant Produkte (Deutschland) GmbH)

Table 3		
Bleaching of palm oil (bleaching with 1.6% by weight of bleaching earth, 0.02% H ₃ PO ₄ at 120°C and 100 mbar for 20 min; deodorization at 240-270°C and < 1 mbar for 120 min))		
Sample	Bleaching	Deodorization
	CV red (1/4" cuvette)	CV red (5/4" cuvette)
Tonsil® Supreme 112 FF (comparative material)	7.4	2.5
Specimen 2.2 (34.8% water) (inventive)	17.9	2.1
Specimen 2.2 (8.9% water) (comparative specimen)	15.6	2.1

In the bleaching of palm oil, raw clays which had been sun-dried (residual water content 34.8%) and dried to a water content of about 9% by weight showed identical results – even though the sun-dried materials have less active material for the same dosage (i.e. are basically “more dilute”). Even compared to the SMBE Tonsil® Supreme 112 FF (as a representative of high-quality standard bleaching earths), the sun-dried clay showed excellent results after the deodorization.

Example 3: Bleaching effect for various vegetable oils

The raw clays from example 2 were additionally processed by adding 3% citric acid (H_3Cit) and mixing until attainment of a homogeneous mass to give DMBEs, and the bleaching effect was tested on various vegetable oils (olive oil, soybean oil, rapeseed oil, sunflower oil). Again, the comparison of sun-dried material (water content 34.8%) was made with “normally” dried material (water content 8.9%) and an SMBE (Tonsil® Supreme 112 FF, Clariant Produkte (Deutschland) GmbH). The experimental details and the results are compiled in tables 4 to 7.

Table 4				
Bleaching of olive oil (bleaching with 1.50% by weight of bleaching earth at 110°C and 30 mbar for 30 min; deodorization at 240°C and $< 1 \cdot 10^{-3}$ mbar for 60 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	2.6	0.05	2.3	0.00
Specimen 2.2 (8.9% water) + 3% by weight of H_3Cit (comparative specimen)	2.1	0.1	1.6	0.01
Specimen 2.2 (34.8% water) + 3% by weight of H_3Cit (inventive)	3.1	0.19	2.2	0.14

Table 5				
Bleaching of soybean oil (bleaching with 0.30% by weight of bleaching earth at 100°C and 30 mbar for 30 min; deodorization at 220°C and < 1 mbar for 30 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	5.4	0.11	0.8	0.10
Specimen 2.2 (8.9% water) + 3% by weight of H ₃ Cit (comparative specimen)	16.6	0.07	0.6	0.07
Specimen 2.2 (34.8% water) + 3% by weight of H ₃ Cit (inventive)	16.3	0.12	1.0	0.11

Table 6				
Bleaching of rapeseed oil (bleaching with 0.60% by weight of bleaching earth at 110°C and 30 mbar for 30 min; deodorization at 230°C and < 1 mbar for 30 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	1.4	0.03	0.6	0.04
Specimen 2.2 (8.9% water) + 3% by weight of H ₃ Cit (comparative specimen)	8.2	0.03	0.4	0.03
Specimen 2.2 (34.8% water) + 3% by weight of H ₃ Cit (inventive)	3.1	0.04	0.4	0.04

Table 7				
Bleaching of sunflower oil (bleaching with 1.00% by weight of bleaching earth at 100°C and 100 mbar for 30 min; deodorization at 240°C and $< 1 \cdot 10^{-3}$ mbar for 60 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	1.4	0.01	1.3	0.002
Specimen 2.2 (8.9% water) + 3% by weight of H ₃ Cit (comparative specimen)	1.6	0.01	1.2	0.004
Specimen 2.2 (34.8% water) + 3% by weight of H ₃ Cit (inventive)	1.8	0.06	1.3	0.03

The product of the invention (i.e. the dry-modified bleaching earth DMBE having a high residual water content of 34.8%) surprisingly exhibited good to very good values after deodorization.

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Example 4: Bleaching effect for various residual water contents

Here, the behavior of the product having relatively high water content with respect to rapeseed oil, which is important in central Europe, was examined. The water content was varied between 8.9% and 34.8%, and it was found that, surprisingly, the bleaching effect improved with increasing water content (decreasing red value). After the deodorization, the red values – irrespective of the water content – were all at an excellent level.

15 The raw clays of example 2 were additionally processed by addition of 3% citric acid (H₃Cit) as described in example 3 to give DMBE and the bleaching effect was tested for rapeseed oil. Again, the comparison of sun-dried material (water content 21% to 34.8%) was made with “normally” dried material (water content 8.9%) and an HPBE (Tonsil®

Supreme 112 FF, Clariant Produkte (Deutschland) GmbH). The experimental details and the results are compiled in table 8.

Table 8				
Bleaching of rapeseed oil (bleaching with 0.60% by weight of bleaching earth at 110°C and 30 mbar for 30 min; deodorization at 230°C and < 1 mbar for 30 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	1.4	0.03	0.6	0.04
Specimen 2.2 (8.9% water) + 3% by weight of H ₃ Cit (comparative specimen)	8.2	0.03	0.4	0.03
Specimen 2.2 (21.0% water) + 3% by weight of H ₃ Cit (inventive)	4.0	0.02	0.4	0.03
Specimen 2.2 (25.3% water) + 3% by weight of H ₃ Cit (inventive)	3.6	0.02	0.4	0.02
Specimen 2.2 (30.5% water) + 3% by weight of H ₃ Cit (inventive)	3.3	0.02	0.4	0.03
Specimen 2.2 (34.8% water) + 3% by weight of H ₃ Cit (inventive)	3.1	0.04	0.4	0.04

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Example 5: Bleaching effect for different acid activation

Analogously to example 3, the raw clay was activated with various solid organic acids. The raw clay was processed by addition of 3% solid organic acid (citric acid, malic acid,

tartaric acid) to give DMBEs and the bleaching effect was tested for rapeseed oil. Again, the comparison of sun-dried material (water content 34.8%) was made with “normally” dried material (water content 8.9%) and an HPBE (Tonsil® Supreme 112 FF, Clariant Produkte (Deutschland) GmbH). The experimental details and the results are compiled

5 in table 9.

Table 9				
Bleaching of rapeseed oil (bleaching with 0.60% by weight of bleaching earth at 110°C and 30 mbar for 30 min; deodorization at 230°C and < 1 mbar for 30 min)				
Sample	Bleaching		Deodorization	
	CV red	Chlorophyll A (ppm)	CV red	Chlorophyll A (ppm)
Tonsil® Supreme 112 FF (comparative material)	1.4	0.03	0.6	0.04
Specimen 2.2 (8.9% water) + 3% by weight of citric acid (comparative specimen)	8.2	0.03	0.4	0.03
Specimen 2.2 (34.8% water) + 3% by weight of citric acid (inventive)	3.1	0.04	0.4	0.04
Specimen 2.2 (8.9% water) + 3% by weight of malic acid (comparative specimen)	3.8	0.01	0.4	0.03
Specimen 2.2 (34.8% water) + 3% by weight of malic acid (inventive)	2.7	0.03	0.6	0.04
Specimen 2.2 (8.9% water) + 3% by weight of tartaric acid (comparative specimen)	4.7	0.01	0.4	0.02

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Specimen 2.2 (34.8% water) + 3% by weight of tartaric acid (inventive)	1.7	0.02	0.5	0.03
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It has been found that, surprisingly, it was possible to distinctly improve the bleaching effect by substituting citric acid with malic acid and especially tartaric acid. The improvement was far more marked in the case of the sun-dried material (34.8% water) than in the case of the product with a normal water content (8.9% water). The higher water content surprisingly promotes the bleaching action of the DMBE.

Patentkrav

1. Fremgangsmåde til fremstilling af en blegejord omfattende følgende trin
- tørring af en vandrig råler til et reduceret vandindhold,
 - 5 - blanding af råleret med reduceret vandindhold med 1-5 vægt-% (i forhold til rålerets vægt) af en fast organisk og/eller koncentreret uorganisk syre,
 - formaling af blandingen af råler med reduceret vandindhold og fast organisk og/eller koncentreret uorganisk syre,
- kendetegnet ved, at** blegejorden har et vandindhold på 20 til 40 vægt-%.
- 10
2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** det vandrige råler har et vandindhold på 50 til 70 vægt-%.
3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** blegejorden har
- 15 et vandindhold på 30 til 40 vægt-%.
4. Fremgangsmåde ifølge et af kravene 1 til 3, **kendetegnet ved, at** den faste organiske syre er udvalgt fra gruppen omfattende citronsyre, æblesyre og vinsyre.
- 20
5. Fremgangsmåde ifølge et af kravene 1 til 3, **kendetegnet ved, at** den koncentrerede uorganiske syre er udvalgt fra gruppen omfattende svovlsyre og phosphorsyre.
- 25
6. Fremgangsmåde ifølge et af kravene 1 til 5, **kendetegnet ved, at** andelen af fast organisk syre hhv. koncentreret uorganisk syre er 1-3 vægt-% i forhold til rålerets vægt.
- 30
7. Fremgangsmåde ifølge et af kravene 1 til 6, **kendetegnet ved, at** det vandrige råler indeholder en smectit-silicagel-blandefase.

8. Blegejord, der kan opnås ved hjælp af fremgangsmåden ifølge krav 7.

9. Anvendelse af blegejorden ifølge krav 8 til raffinering af fedtstoffer og/eller olier.

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10. Fremgangsmåde til raffinering af fedtstoffer og/eller olier, hvor

- der tilvejebringes en råolie, som er udvundet af vegetabilsk eller animalsk materiale,

- råolien underkastes en blegning, idet den behandles med en blegejord ifølge krav 8, og

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- den blegede olie frasepareres fra blegejorden.