United States Patent Office 3,036,102
Patented May 22, 1962



3,036,102

# PROCESS FOR BLEACHING OFF-COLOR COTTONSEED OILS

Walter A. Pons, Jr., and James C. Kuck, New Orleans, and Vernon L. Frampton, Metairie, La., assignors to the United States of America as represented by the Secretary of Agriculture

No Drawing. Filed Aug. 15, 1960, Ser. No. 49,804
1 Claim. (Cl. 260—424)
(Granted under Title 35, U.S. Code (1952), sec. 266)

A nonexclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to a novel process for the bleaching of refined cottonseed oils to remove fixed red color bodies from off-grade or unbleachable cottonseed oils in order to produce oils of acceptable color values without producing deleterious effect on the characteristics or the keeping quality of the oils.

Refined cottonseed oils are customarily treated with adsorbents for the purpose of removing oil-soluble coloring matters which remain in the oil after the usual alkali refining treatment of crude oils. The process is one of adsorption, and is commonly referred to as adsorption bleaching, or bleaching. Adsorbents for this purpose are generally various types of naturally occurring clays which have the property of adsorbing coloring matter from oils. These are used either in the natural state or after suitable activation with mineral acids, and are commonly referred to as natural or activated bleaching earths.

In the case of cottonseed oil, reactions which occur between gossypol, the principal pigment of the seed, and other seed constituents, yield red color bodies which are not removed from the oil by alkali refining and bleaching techniques normally applied to cottonseed oil. Oils in which such color bodies occur are referred to by the industry as off-colored or unbleachable defined oils.

The presence of these color bodies in refined cottonseed oils constitutes a serious problem in the cottonseed processing industry since darkly colored oils are discriminated against. In an effort to improve the color of these unbleachable oils, drastic alkali re-refining has been widely used by the cottonseed industry. The drastic conditions used result in increased loss of oil due to saponification by the alkali and to oil entrainment in the soapstocks. In addition dual refining imposes an added cost to cottonseed processing. Moreover these drastic conditions are not fully effective, since in many cases the red fixed color bodies are not removed by re-refining.

A primary object of the present invention is to provide a novel bleaching process for the removal of fixed red color bodies from refined off-colored or unbleachable cottonseed oils.

Another objective is to provide a novel bleaching process for the removal of easily bleachable pigments from refined cottonseed oil.

Another objective is to provide a bleaching process to produce finished cottonseed oils in which the characteristics and the keeping quality are comparable to those of refined and bleached oils produced by conventional methods.



Another objective is to provide an activated alumina adsorbent which, under certain conditions of use, removes the fixed color bodies from off-colored or unbleachable cottonseed oils.

Another objective is to provide a process for bleaching off-colored or unbleachable oils and which is adaptable to use with conventional plant equipment customarily employed for the bleaching of vegetable oils.

Crude cottonseed oils obtained from mechanical pressing or solvent extraction of cottonseed are usually treated in commercial operation with suitable concentrations of aqueous alkali to remove from the oil the major portion of the nonglyceridic constituents such as fatty acids, resins, phosphatides and various ill defined mucilaginous substances. Cottonseed oils treated in this manner are commonly referred to in the trade as refined oils. Refined oils contain varying amounts of poorly defined alkali-insoluble pigments.

In order to produce oils of acceptably low color values, refined cottonseed oils are treated commercially with adsorbents such as fuller's earths and bentonites to reduce the concentrations in the oil of pigments which are not removed in the refining process. This process is referred to in the trade as the bleaching process. Fuller's earths and bentonites, variously treated, are referred to hereinunder as natural or acid activated bleaching earths.

As customarily performed in the industry, bleaching is conducted on either a batchwise or continuous basis. In the batchwise system the appropriate quantity of fuller's earth or bentonite, is mixed with the oil and the resulting mixture is heated to a temperature ranging from about 70° C. to 140° C. The temperature selected depends upon the type of oil and adsorbent, and on whether the system is exposed to the atmosphere or if it is under vacuum. The heated adsorbent-oil mixture is stirred for periods of time necessary to establish equilibrium, usually 20–40 minutes. The adsorbent is then removed by suitable filtration or centrifugal methods.

In the continuous bleaching system, oil and adsorbent are mixed, heated, and separated by filtration on a continuous basis in closed systems under vacuum.

In the instant invention, 100 parts of refined cottonseed oil are mixed with 1–6 parts of activated alumina comminuted to pass a 400 mesh screen and which contains at least 10% by weight of moisture. The mixture is then stirred mechanically and heated to a temperature of about 225° C. as quickly as practical and held at this temperature for 5–30 minutes. The mixture is then cooled to about 75° C. and the adsorbent is removed by a suitable filtration method. The entire operation consisting of heating and filtration can be conducted under prevailing atmospheric conditions, under an inert atmosphere such as nitrogen, or under vacuum.

Activated aluminas are a porous form of aluminum oxide of high surface area and are produced commercially by controlled calcination of hydrates of aluminum oxide. As usually employed, activated aluminas are essentially anhydrous and are widely used in the form of large granules, rods, or spheres, as desiccating agents for gases and liquids, and they are used in various granular states as catalysts for a variety of chemical reactions. These materials are produced by numerous manufacturers and are readily available. We have found, however, that as usually produced, these activated aluminas are relatively

inefficient for removing fixed red pigments from off-colored cottonseed oils. They are only efficient when utilized under the conditions set forth in the instant invention. Additionally we have found that common forms of aluminas such as calcined and hydrated aluminas, aluminum hydroxide and aluminum silicate are markedly less effective than activated aluminas for the bleaching of cottonseed oils.

The relative efficiency of various types of aluminas for bleaching of an off-colored refined cottonseed oil are illustrated by the results shown in Table I where the color indices recorded are those obtained by the method of W. A. Pons, J. C. Kuck, and V. L. Frampton, "Color Index for Cottonseed Oils," in press Journal of the American Oil Chemists Society, 1960. This color index is the area under the optical density-wave length curve in the region of 400–550 millimicrons. High quality refined and bleached cottonseed oil have color indices of 15–30 according to this method of estimating color indices. Samples of oil were bleached in accordance with the operational procedure set forth in the instant invention. Three types of commercial activated alumina, commercial calcined and hydrated alumina, pure aluminum hydroxide, and synthetic aluminum silicate were used. For comparison purposes the oil was also bleached with both natural and activated bleaching earths, adsorbents which are customarily used to bleach vegetable oils. The data set forth in Table I demonstrate that activated aluminas are superior to conventional bleaching earths, to aluminum salts and to calcined and hydrated aluminas for the bleaching of off-color refined cottonseed oil.

TABLE I

*Efficiency of Adsorbents for Bleaching of Off-Colored Refined Cottonseed Oil*

| Adsorbent | Bleaching conditions [1] | | | | |
|---|---|---|---|---|---|
| | Adsorbent concentration, percent | Particle size (Mesh) | Moisture content, percent | Bleaching temperature, ° C. | Oil color |
| None—Refined oil | | | | | 124.8 |
| Natural bleaching earth | 4.0 | Powd. | | 120 | 62.3 |
| Activated bleaching earth | 4.0 | Powd. | | 120 | 52.8 |
| Aluminum hydroxide | 4.0 | Powd. | | 225 | 80.9 |
| Aluminum silicate | 4.0 | −400 | 10.5 | 225 | 51.5 |
| Calcined alumina | 4.0 | −325 | Dry | 225 | 66.9 |
| Hydrated alumina | 4.0 | [2] 5–10 | 34.9 | 225 | 52.9 |
| Activated alumina #A | 4.0 | −325 | Dry | 225 | 46.1 |
| Do [3] | 4.0 | −325 | 10.4 | 225 | 33.4 |
| Activated alumina #B [3] | 4.0 | −400 | 13.2 | 225 | 32.8 |
| Activated alumina #C [3] | 4.0 | −400 | 22.9 | 225 | 28.0 |

[1] 5 minute contact time at specified temperature.
[2] Microns.
[3] Air equilibrated.

We have found that the effectiveness of activated alumina as a bleaching agent is also dependent on its moisture content, on the particle size of the adsorbent and the temperature of bleaching. The effect of contact time of the adsorbent is not critical. The importance of the first three variables, and the effect of each when the other two are held constant is illustrated by the data set forth in Tables II and III. It may be noted from the data (Table II) that when the amount of adsorbent, particle size, moisture content and contact time are held constant, optimum color reduction is attained at bleaching temperatures of 225° C. or higher. To avoid damage to the oil it is preferred to conduct bleaching at no higher than 225° C.

The effect of varying the moisture content of the alumina when the variables of adsorbent concentration, particle size, bleaching temperature and contact time are held constant (Table II) indicates that alumina adsorbents are most efficient when the moisture content is at least 10% by weight.



TABLE II

*Effect of Bleaching Temperature, and Moisture Content of Alumina on Bleaching Efficiency of Activated Alumina*

| Variable temperature | | Variable moisture | |
|---|---|---|---|
| Bleaching temperature, [1] ° C. | Oil color | Moisture content of alumina, [2] percent | Oil color |
| 26 | 74.7 | Dry | 46.1 |
| 75 | 66.5 | 1.41 | 47.1 |
| 120 | 64.4 | 4.69 | 40.7 |
| 150 | 64.1 | 5.64 | 37.7 |
| 200 | 48.0 | 6.72 | 37.0 |
| 225 | 31.1 | 10.42 | 33.7 |
| 260 | 30.1 | 13.36 | 32.6 |

[1] 4% alumina (−400 mesh) containing 10.4% water in each bleach, 5 minute contact time at designated temperature.
[2] 4% alumina (−325 mesh) of designated moisture content in each bleach; 5 minute contact time at 225° C. in each case.

When the moisture content, amount of adsorbent, contact time and bleaching temperature are held constant, and the particle size of the alumina is varied, results shown in Table III demonstrate that the effectiveness of activated alumina in removing red fixed color bodies from off-colored or unbleachable oils increases with the degree of subdivision of alumina particles. We prefer to use 400 mesh alumina, since filtration difficulties are encountered with more finely divided material.

TABLE III

*Effect of Particle Size and Bleaching Time on Bleaching Efficiency of Activated Alumina*

| Variable particle size | | Variable bleaching time | |
|---|---|---|---|
| Mesh range of activated alumina [1] | Oil color | Contact time at 225°C.,[2] min. | Oil color |
| −100; +200 | 56.2 | 5 | 31.1 |
| −200; +270 | 48.6 | 10 | 32.7 |
| −270; +320 | 42.5 | 15 | 32.9 |
| −400 | 35.0 | 20 | 33.4 |
| | | 25 | 31.7 |

[1] 4% alumina of designated particle size in each bleach; 5 min. contact time at 225°C.
[2] 4% alumina (−400 mesh) containing 10.4% water in each bleach; designated contact time at 225°C. in each case.

The contact time of the adsorbent is not critical, as the data shown in Table III indicate that variation from 5 to 25 minutes has no marked effect on the color index of the bleached oil. The short contact time required, less than 5 minutes, indicates that the bleaching process is adaptable to continuous bleaching, where oil and adsorbent are continuously mixed, heated and filtered.

The amount of activated alumina used in the bleaching of off-colored oils depends on the amount of color reduction desired.

Actually, the adsorption of the red color bodies on activated alumina follows the Freundlich adsorption isotherm, and the red color intensity of the bleach oil decreases with increasing quantity of alumina used.

From the data set forth in Table IV where the quantity of natural and acid actuated bleaching earth and of activated alumina is varied from 1 to 6 percent of the weight of the oil in the bleaching of a sample of off-colored refined cottonseed oil, it can be seen that 2 percent of activated alumina produces greater color reduction than 6 percent of conventional bleaching earths.

We have found that the oil entrainment on activated alumina is comparable to that observed for the conventional adsorbents such as natural bleaching earth.

We have also found that the recovery of adsorbed or retained glycerides from the spent alumina adsorbent,

and the re-activation of the adsorbent for repeated use are readily accomplished. Neutral glycerides retained by the adsorbent are approximately 25 percent of the weight of the adsorbent, and are readily removed by solvents such as commercial hexane. The recovered oil, after solvent removal, is of a quality comparable to the alumina bleached oil recovered by filtration.

Strongly adsorbed materials such as fatty acids and color bodies are not removed by solvent extraction. These are oxidized by heating the spent adsorbent to 550–600° C. in the presence of air. After equilibration to the optimum moisture level, the regenerated adsorbent is suitable for reuse as a bleaching agent. The reactivation process can be repeated indefinitely.

TABLE IV

*Effect of Adsorbent Concentration on Bleaching of Off-Color Refined Cottonseed Oil*

| Adsorbent concentration in bleach, percent | Bleached oil color | | |
|---|---|---|---|
| | Natural bleaching earth [1] | Acid activated bleaching earth [1] | Activated alumina [2] |
| 1 | 75.6 | 77.0 | 46.0 |
| 2 | 68.3 | 66.5 | 34.3 |
| 3 | 62.4 | 59.4 | 31.1 |
| 4 | 60.4 | 52.8 | 29.0 |
| 5 | 61.2 | 46.7 | 27.8 |
| 6 | 53.6 | 44.4 | 26.1 |

[1] Commercial grade, standard AOCS bleach test.
[2] Commercial alumina ground to pass a 400 mesh screen, equilibrated to 22.9% moisture. 5 minute bleaching time at 225° C. in each case.

The following examples are illustrative of details of at least one method of practicing the invention.

EXAMPLE 1

Seven samples of refined off-colored cottonseed oils were used in these experiments.

To 100 parts by weight of each of the seven oils (Table V) were added 4 parts of a commercial activated alumina which had been ground to pass a 400 mesh screen and which contained 17.6 percent water. Each oil and alumina mixture was stirred continuously under prevailing atmospheric conditions, and the mixture was heated rapidly to 225° C. The mixture was held at 225° C. for 5 minutes, cooled to about 75° C. and filtered.

Portions of each refined oil were also bleached by following the operational procedure of the American Oil Chemists' Society Official and Tentative Methods where fuller's earth (Official AOCS earth for 1960) was used.

The color indices of the bleached oils were determined and are recorded in Table V. In all cases improvement in color of the oils bleached with alumina was much greater than that obtained with fuller's earth.

TABLE V

*Improvement in Bleach Color of Off-Colored Refined Cottonseed Oils by Use of Activated Alumina Bleaching*

| Oil No. | Type of refined off-colored cottonseed oil | Refined oil color | Bleach color | |
|---|---|---|---|---|
| | | | A.O.C.S. bleach test [1] | Activated alumina bleach [2] |
| 1 | Expeller | 219 | 82.4 | 56.9 |
| 2 | Screw-pressed | 125 | 62.3 | 30.2 |
| 3 | Re-refined, expeller | 171 | 48.3 | 35.9 |
| 4 | Expeller | 104 | 46.3 | 30.6 |
| 5 | Screw-pressed | 130 | 52.6 | 31.5 |
| 6 | do | 147 | 56.5 | 28.8 |
| 7 | Under-refined, screw-press | 134 | 26.5 | 19.9 |

[1] Official bleaching test of American Oil Chemists' Society.
[2] Commercial activated alumina ground to pass a 400 mesh screen, equilibrated to 17.6% moisture. 4% alumina in each bleach, 5 minute contact time at 225° C.



EXAMPLE 2

A sample of a refined unbleachable off-colored cottonseed oil, and a sample of refined prime bleachable grade cottonseed oil were each bleached with 4 percent activated alumina as outlined in Example 1. They were then deodorized by use of laboratory scale deodorization equipment. For control purposes, oils were also bleached with 4 percent natural bleaching earth as described in the official and tentative methods of the AOCS and were also subjected to the identical deodorization technique. The results shown in the following table illustrate that there is a reduction in color index on deodorization of both off-color and bleachable cottonseed oils. This reduction in the color index due to deodorization conditions is well known in the trade. The results demonstrate that for off-color oils, the reduction after conventional bleaching is not sufficient to produce oils of desirably low color.

The results for Oil B, a bleachable oil, demonstrate that activated alumina is also effective for bleaching oils of this type. Although the invention is primarily designed to improve the color of off-color or unbleachable cottonseed oils, it may, if desired, be applied also to easily bleachable refined cottonseed oils to produce oils having color values comparable to those obtained by use of conventional adsorbents.

*Example 2.—Effect of Bleaching and Deodorization on Cottonseed Oil Color*

| Type of refined cottonseed oil | Natural earth | | Activated alumina | |
|---|---|---|---|---|
| | Bleach color | Deodorized color | Bleach color | Deodorized color |
| A. Off-color | 57.8 | 45.4 | 35.8 | 28.3 |
| B. Bleachable | 14.3 | 7.0 | 15.8 | 5.1 |

EXAMPLE 3

A single sample of refined cottonseed oil was bleached with 4 percent activated alumina as outlined in Example 1 under prevailing atmospheric conditions. Another sample of the same refined oil was also bleached with 4 percent of activated alumina under conditions where the entire heating and cooling period before filtration were conducted under vacuum. For control purposes, another sample of the same oil was bleached with 4 percent natural earth using the standard bleaching test of the American Oil Chemists Society.

The refined oil and the three bleached oils were examined to determine the effect of the alumina bleaching on the oil properties.

*Example #3.—Effect of Bleaching on Oil Properties*

| Oil property | Refined oil only | Bleached oil | | |
|---|---|---|---|---|
| | | Natural bleaching earth bleach | Activated alumina bleach | |
| | | | Atmospheric bleach | Vacuum bleach |
| Iodine number | 104.5 | 104.7 | 104.4 | 104.4 |
| Refractive index $N_D^{25°}$ C | 1.4698 | 1.4699 | 1.4700 | 1.4699 |
| Unsaponifiable matter, percent | 0.57 | 0.53 | 0.59 | 0.55 |
| Tocopherols, percent | 0.053 | 0.055 | 0.056 | 0.056 |
| Keeping time, hrs.[1] | 22.5 | 36.0 | 40.5 | 35.0 |
| Absorptivity: | | | | |
| 233 mu (diene conjugation) | 0.400 | 0.255 | 0.681 | 0.570 |
| 268 mu (triene conjugation) | 0.019 | 0.222 | 0.115 | 0.076 |
| 315 mu (tetraene conjugation) | 0.0015 | 0.0083 | 0.0083 | 0.0065 |

[1] Oven stability at 100° C.; time in hrs. for oil to reach peroxide value of 100.

The results of the analysis of the oil, as recorded in the

accompanying table, indicate that the alumina bleaching technique has no adverse effect on oil properties. Compared with the properties of the oil bleached with conventional bleaching earth, the unsaturation (iodine number, and refractive index), antioxidants (tocopherols), keeping time, and fatty acid conjugation (diene, triene, and tetraene conjugation) of the alumina bleached oil are equivalent. In addition, the properties of the oil bleached with alumina under atmospheric conditions are essentially equivalent to the alumina bleaching conducted under vacuum. Thus the effect of atmospheric oxidation is not significant for the alumina bleaching technique, and the process is adaptable to either batchwise bleaching under atmospheric conditions or to continuous bleaching under vacuum.

We claim:

A process for bleaching refined off-color cottonseed oil comprising treating the refined off-color cottonseed oil



at a temperature of about 225° C. with activated alumina comminuted to pass a 400 mesh screen, said activated alumina containing at least 10% by weight of moisture, and separating the alumina from the resulting mixture to obtain a bleached refined cottonseed oil of acceptable color value and having characteristics and keeping qualities substantially the same as those of the oil prior to said treatment thereof.

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