(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 September 2016 (15.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/142953 A2

(51) International Patent Classification:
C11B 3/12 (2006.01)

(21) International Application Number:
PCT/IN2016/000060

(22) International Filing Date:
3 March 2016 (03.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
780/MUM/2015 10 March 2015 (10.03.2015) IN
201621007004 29 February 2016 (29.02.2016) IN

(71) Applicant: **PRAJ INDUSTRIES LIMITED** [IN/IN]; Praj Tower, Bhumkar Chowk - Hinjewadi Road, Hinjewadi, Pune-411057 (IN).

(72) Inventor: **KULKARNI, Mangehs Ganesh**; Praj Tower Industries Limited, Bhumkar Chowk - Hinjewadi Road, Hinjewadi, Pune-411057 (IN).

(74) Agent: **PARAG, Kinge**; Praj Tower INDUSTRIES LIMITED, Bhumkar Chowk - Hinjewadi Road, Hinjewadi, Pune-411057 (IN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2016/142953 A2

(54) Title: METHOD FOR THE PURIFICATION OF WAXES

(57) Abstract: The invention relates to a method for the purification of crude rice bran and sunflower waxes using an alcohol as a purifying solvent. It particularly relates to the use of ethyl alcohol as said solvent for efficient and economic purification of crude rice bran and sunflower waxes into economically valuable high purity wax products.

METHOD FOR THE PURIFICATION OF WAXES

FIELD OF INVENTION

The invention relates to a method for the purification of crude rice bran and sunflower waxes using an alcohol as a purifying solvent. It particularly relates to the use of ethyl alcohol as said solvent for efficient and economic purification of crude rice bran and sunflower waxes into economically valuable high purity wax products.

BACKGROUND

Rice is one of the most important grains in the world and India is second largest producer of it. The rice bran is a valuable by-product of rice milling industry. It is recently used for prepare edible rice bran oil as a valuable product. The bran contains about 12% to 25% oil component. Beside oil, the bran also contains about 5% waxy materials called rice bran wax, which is by-product of rice bran oil refining process. The crude wax has certain low value applications; however if purified to certain higher degree it forms a valuable product as being used in cosmetics and food preparations.

Chemically the rice bran wax is a heterogeneous product with made up of saturated monoesters of long chain fatty acid [C-22 to C-26] and long chain fatty alcohols [C-26 to C-30]. Up on refining or purification the wax becomes a relatively homogenous mixture having physical characters like melting point of about 78 °C to 82 °C , saponification value of about 70 to 120 units and iodine value of about 4 to 10 units.

This purified rice bran wax then has many industrial applications like leather polishes, crayons, candles, shoe creams, paper coatings, carbon papers, lubricants etc. Other major applications are in food industry like in chocolate enrobes, vegetable coatings and wax emulsions for fruit preservation. It is further used in pharmaceuticals products like tablets, ointments, suppositories and cosmetic products like moisturizing lotions, lipsticks, skin creams etc.

In the prior art one of the methods the rice bran wax is purified or refined is by removing the residual oil from it by hydraulic pressing to maximum extent possible, followed by extracting it in solvents like isobutanol or isopropanol with water. However, these extractions are costly for recycling of isobutanol or isopropanol in the process is expensive and efficiency of the process is limited. As the crude rice bran wax contains about 10% to 50% resinous materials besides the oil, its purification greatly increases its value and applicability. The disclosed invention describes a novel method of purification of crude rice bran wax to high purity waxes.

BRIEF DESCRIPTION OF THE INVENTION

The disclosure provides a method for purifying crude rice bran wax comprising: mixing said wax with ethanol forming a mixture; refluxing said mixture for a desired time dissolving said wax; allowing said mixture to stand idle for desired time; separating undissolved matters from liquid fraction; cooling said liquid fraction allowing formation of crystallised wax; removing said crystallised wax by filtration; washing

said crystallised wax by ethanol; repeating steps above up to four times with said undissolved matters to extract remaining wax; and pooling and drying said crystallised wax under vacuum forming a final product that is a purified rice bran wax with consistent characters of physical and chemical properties

The disclosure provides a method for purifying crude sunflower wax comprising: mixing said wax with ethanol forming a mixture; refluxing said mixture for a desired time dissolving said wax; allowing said mixture to stand idle for desired time; separating undissolved matters from liquid fraction; cooling said liquid fraction allowing formation of crystallised wax; removing said crystallised wax by filtration; washing said crystallised wax by ethanol; repeating steps above up to three times with said undissolved matters to extract remaining wax; and pooling and drying said crystallised wax under vacuum forming a final product that is a purified sunflower wax with consistent characters of physical and chemical properties

DETAILED DESCRIPTION OF THE INVENTION

In an embodiment of the invention, the crude rice bran wax obtained as a by-product of rice bran oil refining process is dissolved in absolute ethyl alcohol. In the first step, about five parts of ethanol and one part the wax is refluxed at about 75 °C in a reflux vessel for about 1 hour to allow dissolution of rice bran wax into ethanol leaving resinous impurities undissolved in the mixture. The oil present in the crude is also dissolved in ethanol. After refluxing the mixture, the

liquid fraction is decanted and allowed to cool to room temperature for the wax to crystallize out from the solution. Then the solid wax is removed by filtration under vacuum, one washed with ethanol, optionally decoloured with an oxidizing agent, and dried to get the white to pale yellow solid mass of purified rice bran wax having consistent physical and chemical properties like melting temperature and purity. The resinous matters obtained are further subject to ethanol refluxing to recover remaining wax up to 4 times, if required. On average, the crude rice bran wax contains up to 50% oil, which is obtained as a by-product of the process disclosed herein. Further remaining resinous matters may also be as crude waxy material.

In another embodiment of the invention, the crude sunflower wax obtained as a byproduct of the sunflower oil refining process is dissolved in absolute ethyl alcohol. In the first step, about five parts of ethanol and one part the wax is refluxed at about 75 °C in a reflux vessel for about 1 hour to allow dissolution of said wax into ethanol leaving impurities undissolved in the mixture. The oil present in the crude is also dissolved in ethanol. After refluxing the mixture, the liquid fraction is decanted and allowed to cool to room temperature for the wax to crystallize out from the solution. Then the solid wax is removed by filtration under vacuum, once washed with ethanol, optionally decoloured with an oxidizing agent, and dried to get the white to pale yellow solid mass of purified sunflower wax having consistent physical and chemical properties like melting temperature and purity. The impurities/ residues obtained are further subject to

ethanol refluxing to recover remaining wax up to 3 times, if required. On average, the crude sunflower wax contains up to 40% oil, which is obtained as a byproduct of the process disclosed herein. Further remaining residues may also be as crude waxy material.

In another embodiment of the invention, ethanol used as the solvent for refluxing of the crude rice bran or sunflower wax is absolute ethanol or ethanol at least 99% pure by volume. Any reduction in the purity of ethanol below 99% leads to drastic reduction in the final yield of purified said waxes as the presence of water in ethanol leads to reduction in the dissolution of waxes in ethanol.

In yet another embodiment of the invention, the refluxing of said waxes and ethanol mixture is performed for at least one hour at temperature about 75 ^{0}C with an efficient condenser to prevent loss of the solvent.

In further embodiment of the invention, the said purified waxes are used in preparation of pharmaceutical or cosmetic products that required unique characters of the wax like its melting temperature, texture, colour, etc.

ADVANTAGES OF THE DISCLOSED PROCESS:

- The disclosed process is simple, carried out in two vessels, and hence is scalable for the large volume applications.
- The steps used for recovery are simple and efficient due to simplicity of the process.

- The disclosed process is substantially more economical compared with earlier processes.
- Ethanol is recycled in the process after simple pretreatment.

EXAMPLES

Examples provided below give wider utility of the invention without any limitations as to the variations that may be appreciated by the person skilled in the art. A non-limiting summary of various experimental results is given in the examples, which demonstrate the advantageous and novel aspects of the process disclosed herein.

EXAMPLE 1

About 100 g of crude rice bran wax containing oil and resinous matter impurities was taken in a refluxing vessel with about 500 mL of ethanol [99.9% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved resinous matters were again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL, 300 mL and 200 mL respectively to remove any undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at room temperature, allowed to stand idle for

dissolved wax to crystallize out from oil and other impurities, and then separated by vacuum filtration. Said crystallized wax was once washed with about 100 mL of ethanol and dried under vacuum to form the final wax product [purified rice bran wax]. These steps afforded about 36 g of highly pure final wax product with acid value of about 6.5 units, saponification value of about 84 units and iodine value of about 16 units with white to pale yellow coloration. Further, about 40 g of oil and about 22 g of solid resinous matters were recovered as by-products.

EXAMPLE 2

About 100 g of crude rice bran wax containing oil and resinous matter impurities was taken in a refluxing vessel with about 500 mL of ethanol [98% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved resinous matters were again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL, 300 mL and 200 mL respectively to remove any undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at room temperature, allowed to stand idle for dissolved wax to crystallize out from oil and other impurities, and

then separated by vacuum filtration. Said crystallized wax was once washed with about 100 mL of ethanol and dried under vacuum to form the final wax product [purified rice bran wax]. These steps afforded about 18 g of highly pure final wax product with acid value of about 7 units, saponification value of about 82 units and iodine value of about 15 units with white to pale yellow coloration. Further, about 39 g of oil and about 41 g of solid resinous matters were recovered as by-products.

EXAMPLE 3

About 100 g of crude rice bran wax containing oil and resinous matter impurities was taken in a refluxing vessel with about 500 mL of ethanol [95% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved resinous matters were again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL, 300 mL and 200 mL respectively to remove any undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at room temperature, allowed to stand idle for dissolved wax to crystallize out from oil and other impurities, and then separated by vacuum filtration. Said crystallized wax was once

washed with about 100 mL of ethanol and dried under vacuum to form the final wax product [purified rice bran wax]. These steps afforded about 12 g of highly pure final wax product with acid value of about 7.5 units, saponification value of about 83 units and iodine value of about 23 units with white to pale yellow coloration. Further, about 34 g of oil and about 50 g of solid resinous matters were recovered as by-products.

EXAMPLE 4

About 100 g of crude sunflower wax containing residual oil impurity was taken in a refluxing vessel with about 500 mL of ethanol [99.9% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved wax along with impurities was again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL and 300 mL respectively to recover the undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at room temperature, allowed to stand idle for dissolved wax to crystallize out from oil and other impurities, and then separated by vacuum filtration. Said crystallized wax was once washed with about 100 mL of ethanol and dried under vacuum to form the final wax

product [purified rice bran wax]. These steps afforded about 48 g of highly pure final wax product with acid value of about 1.5 units, saponification value of about 87 units and iodine value of about 27 units with white to white colour. This product has a melting point of about 80 °C. Further, about 37 g of oil and about 8 g of solid impurities were recovered as byproducts.

EXAMPLE 5

About 100 g of crude sunflower wax containing residual oil impurity was taken in a refluxing vessel with about 500 mL of ethanol [98% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved wax along with impurities was again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL, 300 mL, 200 mL, and 300 mL respectively to recover the undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at 10 °C temperature, allowed to stand idle for dissolved wax to crystallize out from oil and other impurities, and then separated by vacuum filtration. Said crystallized wax was once washed with about 100 mL of ethanol and dried under vacuum to form the final wax product [purified rice bran wax]. These steps

afforded about 31 g of highly pure final wax product with acid value of about 2 units, saponification value of about 71 units and iodine value of about 30 units with white to white colour. This product has a melting point of about 78 °C. Further, about 33 g of oil and about 33 g of solid product were recovered as byproducts.

EXAMPLE 6

About 100 g of crude sunflower wax containing residual oil impurity was taken in a refluxing vessel with about 500 mL of ethanol [95% pure by volume] forming a mixture. Then said mixture was refluxed at about 75 °C for about 1 h to dissolve the wax part and then allowed to stand idle at room temperature for about 30 min to settle the resinous mattes at the bottom of reactor. Next, the top liquid fraction containing mostly wax and oil was decanted and collected in a vessel. The undissolved wax along with impurities was again subjected to the above refluxing steps with reduced amounts of ethanol at each subsequent repeat at 400 mL, 300 mL, 200 mL, and 300 mL respectively to recover the undissolved wax. The liquid fractions after each step were collected and pooled. Next, said liquid fraction pool was cooled at 10 °C temperature, allowed to stand idle for dissolved wax to crystallize out from oil and other impurities, and then separated by vacuum filtration. Said crystallized wax was once washed with about 100 mL of ethanol and dried under vacuum to form the final wax product [purified rice bran wax]. These steps afforded about 24 g of highly pure final wax product with acid value

of about 4 units, saponification value of about 135 units and iodine value of about 61 units with white to white colour. This product has a melting point of about 78 °C. Further, about 26.6 g of oil and about 54.2 g of solid product were recovered as byproducts.

While the invention has been particularly shown and described with reference to embodiments enlisted in examples, it will be appreciated that several of the above disclosed and other features and functions, or alternatives thereof, may be desirably combined into many different systems or applications. Also that various presently unforeseen and unanticipated alternatives, modifications, variations, or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims. Although the invention has been described with reference to specific preferred embodiments, it is not intended to be limited thereto; rather those having an ordinary skill in the art will recognize that variations and modifications may be made therein which are within the spirit of the invention and within the scope of the claims.

CLAIMS

We Claims:

1. A method for purifying crude rice bran or sunflower wax comprising:
    a) mixing said wax with ethanol forming a mixture;
    b) refluxing said mixture for a desired time dissolving said wax;
    c) allowing said mixture to stand idle for desired time;
    d) separating undissolved matters from liquid fraction;
    e) cooling said liquid fraction allowing formation of crystallised wax fraction;
    f) removing said crystallised wax fraction by filtration;
    g) washing said crystallised wax fraction by ethanol;
    h) repeating steps (a) to (g) up to four times with said undissolved matters to extract remaining wax; and
    i) pooling said crystallised wax fractions and drying under vacuum forming a final product.
2. A method of claim 1, wherein purity of ethanol is not less than 95% by volume.
3. A method of claim 1, wherein said refluxing is performed for at least for one hour.
4. A method of claim 1, wherein said refluxing is performed at about 75 °C.
5. A method of claim 1, wherein said liquid fraction is gradually cooled to room temperature.
6. A method of claim 1, wherein said crystallised wax fraction is filtered by vacuum filtration.
7. A method of claim 1, wherein said wax contains between 10% to 50% oil by weight.
8. A method of claim 1, wherein said final product is optionally decoloured using an oxidising agent.

9. A method of claim 1, wherein said final product is clear white to pale yellow in colour upon vacuum drying.
10. A wax product according to claim 1, used in cosmetic or food preparations.